Lompoc Pesticide Air Monitoring
Fumigant Sampling and Analysis Plan
Final Plan Submitted January 3, 2000

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1. INTRODUCTION

1.1 Background

In 1997, the Department of Pesticide Regulation (DPR) formed the Lompoc Interagency Work Group (LIWG) to help investigate Lompoc residents' concerns (first voiced in 1992) about pesticide use as it relates to community health. DPR has sought answers to whether health symptoms in Lompoc (Santa Barbara County) are occurring at a high rate and if so, to determine if pesticides contribute to the problem, or are a part of the cause.

The LIWG is composed of staff from federal, state, county and city agencies as well as community representatives. The LIWG formed several subgroups to develop recommendations to address health concerns, to conduct a pesticide air-monitoring program, and to consider potential exposures from other environmental factors, such as crystalline silica and radon. The pesticide exposure subgroup (now called the Technical Advisory Group) developed a work plan that recommended comprehensive air monitoring in Lompoc during various seasons to determine whether, and in what amounts, pesticides occur in air in residential areas within the city of Lompoc. This exposure subgroup prioritized 46 pesticides based on their toxicity, use, and volatility.

The Technical Advisory Group (TAG) recommended a comprehensive monitoring program to span peak use periods for the top 23 chemicals in a two-phase program. The TAG did not recommend monitoring for the remaining 23 pesticides from the original list of 46, realizing fiscal resources were limited. The first phase of monitoring was recommended for the summer of 1998 (if only partial funding was available), and the second phase for early summer of 1999 (Appendix A). The monitoring recommendation was designed to measure maximum daily pesticide concentrations in air that could be compared to human health endpoints. The LIWG accepted the TAG recommendations and forwarded them to DPR in April 1998.

In August 1998, the Legislature passed Senate Bill 661, which provided funding to DPR to conduct the first phase of pesticide air monitoring. The first phase of monitoring was completed in September 1998 (results are summarized in Section 3.2). In May 1999, DPR received a grant from the U.S. Environmental Protection Agency (U.S. EPA) to monitor fumigant applications in the Lompoc area during fall and winter months. This document describes the monitoring planned for fumigants during the months of November 1999 through January 2000, although potentially monitoring may be conducted in the spring and/or fall 2000.

1.2 Data Quality Objectives for Fumigant Monitoring

1.2.1 *State the Problem*

Develop a Concise Description of the Problem - Lompoc residents have voiced concerns about pesticide use as it relates to community health. An evaluation of available health-related data, including hospital discharges and cancer incidence, suggest that certain respiratory illnesses, such as asthma, bronchitis, and lung and bronchus cancers, occur in Lompoc at higher rates than in other comparison areas. To aid in the evaluation of the effect of pesticides on residents in Lompoc we first need to determine whether, and in what amounts, pesticides occur in ambient air within the city of Lompoc. Since the term pesticide constitutes a large number of chemicals, the measurement of air concentrations will be conducted in phases. In this phase, as described in this sampling and analysis plan, air measurements and model estimates will be made for a group of four pesticides known as fumigants.

Ambient air concentrations of fumigants will be measured within the city of Lompoc and compared with their respective screening levels. The U.S. EPA or California's Office of Environmental Health Hazard Assessment typically generate enforceable human health standards. Human health standards for ambient air have not been developed for these fumigants. DPR has developed screening levels, in consultation with members of the TAG, in the absence of such standards (Appendix B). Screening levels are not equivalent to human health standards and cannot be interpreted as such. However, DPR will use these screening levels as interim action levels until enforceable standards are developed and adopted.

Identify Primary Decision-Maker - As the lead agency for the registration and use of pesticides in California, DPR is the primary decision-maker for this project.

Identify the Members of the Planning Team - DPR formed the Lompoc Interagency Work Group (LIWG) to help investigate Lompoc residents' concerns. The LIWG is composed of staff from federal, state, and county agencies as well as staff from the city of Lompoc and community representatives. The LIWG formed several subgroups to develop recommendations to address health concerns, to conduct a pesticide air monitoring strategy, and to consider potential exposures from other environmental factors, such as crystalline silica and radon. The pesticide exposure subgroup (now called the Technical Advisory Group or TAG) assists in the planning, implementation, and evaluation of pesticide air monitoring in Lompoc. Members of the TAG are listed in Appendix C.

Specify Available Resources and Relevant Deadlines - This project is being conducted in phases due to complexity and funding constraints. This phase of the project focuses on

monitoring for fumigants used in the Lompoc area and is being conducted under a grant from the U.S. EPA (Agreement E-999332-01-5). DPR will use the $80,000 in U.S. EPA grant funds and $20,000 of DPR funds to contract for field sampling and laboratory analysis. See Appendix D for the field sampling and laboratory analysis contracts. (Note: $20,000 from the U.S. EPA grant will be used by the Other Environmental Issues subgroup of the LIWG for a meteorological survey. The sampling protocol for that study will be developed by that subgroup and will not be described here.) Members of the TAG provide in-kind contributions, such as project planning and supervision, compilation of pesticide use data, compilation of meteorological data, evaluation of data, and report preparation and review. Field sampling and laboratory analysis for this phase will occur during the winter of 1999-2000 and potentially continue into spring and fall of 2000.

1.2.2 *Identify the Decision*

Identify the Principal Study Questions - Do ambient air concentrations of fumigants used in the Lompoc valley exceed the acute (24-hour) screening level? (This objective was reiterated during a TAG meeting on October 26, 1999. The major concern of members who voiced an opinion was over acute, not subchronic or chronic levels. However, these levels will be evaluated as described in sections 1.2.3 and 7.1) The fumigants to be monitored, if applied during the months of December, January, and February include 1,3-dichloropropene, chloropicrin, metam sodium, and methyl bromide. (See section 1.2.4 for discussion of fumigant selection.) Extension of fumigant monitoring into April and for a period in the fall of 2000 is currently under discussion with TAG members and the laboratory and field contractors.

Define Alternative Actions-
(a) no action is taken (Table 1).
(b) a more refined analysis is undertaken (Table 1).
(c) regulatory action is taken to reduce fumigant air concentrations (Table 1).

Combine the Principal Study Question and Alternative Actions into a Decision Statement -Determine if fumigant air concentrations are above screening levels and if they are, determine if regulatory actions are required to mitigate them.

1.2.3 *Identify Inputs to the Decision*

Identify the Information Required to Resolve the Decision Statement - There are two primary inputs required to resolve the decision statement, namely, air concentrations of fumigants in Lompoc and acute (24-hour) screening levels for those fumigants. Air concentrations of fumigants in the Lompoc area will be measured directly as well as modeled in this study to generate the data needed to compare with the screening levels.

Acute (24-hour) screening levels have been proposed by DPR toxicologists for each fumigant to be monitored (Appendix B, Table 1). Other information may be useful and/or essential for interpreting pesticide air concentrations, such as subchronic screening levels (Appendix B), meteorological data, and pesticide use records. While there is likely to be pesticide exposure from routes other than air (e.g., through food and water residues that might result from pesticide use) inhalation is of primary concern due to the high volatility of fumigants and documented respiratory illnesses in Lompoc.

Determine the Sources for Each Item of Information - Information on fumigant air concentrations will be obtained by direct measurement during December through February. In addition, modeling will be conducted to supplement air measurements. Pesticide use records from this period indicate a high use of certain fumigants during winter months (Tables 2-4). Monitoring stations will be established in Lompoc to measure fumigant air concentrations during fumigant applications. Information on pesticide use will be obtained from pesticide use reports submitted by pesticide users to the Santa Barbara County Agricultural Commissioner's Office. Meteorological conditions will be measured by the Santa Barbara County Air Pollution Control District at its existing station in Lompoc. In addition, a MetOne® station will be established in the agricultural area west of Lompoc and operated by staff from the DPR.

Confirm that the Appropriate Measurement Methods Exist to Provide the Necessary Data -The most widely used procedure for atmospheric measurement of pesticides is to pass 2 to 100 liters of air per minute through a solid sorbent material onto which the pesticide is adsorbed (Keith, 1988). In addition, lower flow rates (< one L/min) have been used to trap pesticides and prevent breakthrough on sorbent media during air sampling (Ross et al., 1996; Kollman, 1995). Sorbent media typically used to trap pesticides include XAD resins and carbon sorbents such as charcoal (Majewski and Capel, 1995; Keith, 1988; Baker, et al., 1996). Chemical extraction methods for removing fumigants from sorbent media and analyzing with a gas chromatograph equipped with a detector provide quantitation of air concentrations below the acute (24-hour) screening levels and associated decision rules (Table 5).

In addition, canisters have been used as an alternative to solid sorbents for air sampling (Keith, 1988). However, at this time chemical analytical methods for fumigants sampled using canisters are only available for 1,3-dichloropropene and methyl bromide.

1.2.4 *Define the Study Boundaries*

Specify the Characteristics that Define the Population of Interest - The population of interest is the fumigants used in the Lompoc area. Based on pesticide use reports between 1996 and 1998, one fumigant, metam sodium, is used most in the Lompoc area during December, January, and February (Tables 2 - 4). Other fumigants may be used in

the Lompoc area, such as 1,3-dichloropropene, aluminum phosphide, chloropicrin, methyl bromide, and sulfuryl fluoride. Very little aluminum phosphide is used in the Lompoc area (approximately six pounds per year). Therefore, exposure should be low, so it will not be monitored at this time. Sulfuryl fluoride is used for structural fumigations and its use is reported only on a countywide basis. The specific use pattern in the Lompoc area is currently under investigation by the County Agriculture Commissioner's staff. Therefore the TAG decided to defer consideration for monitoring of sulfuryl fluoride to a later date. No other fumigants were reported for the Lompoc area between 1996 and 1998 (DPR 1996, 1997a, 1998). Therefore, fumigant monitoring will include 1,3-dichloropropene, chloropicrin, methyl isothiocyanate (MITC, the biologically-active breakdown product of metam sodium, see section 5.1), and methyl bromide, if applied during the study period.

Define the Spatial Boundary of the Decision Statement – The spatial boundary of the decision statement is the outdoor air within the Lompoc city limit. The city of Lompoc, 11.3 square miles in area, is located in a coastal valley of Santa Barbara County, California, approximately eight miles east of the coastline (Figure 1). The valley is oriented roughly northwest to southeast. Between the city and the ocean lies an agricultural region predominantly devoted to vegetable and flower production. Predominant wind patterns during winter months tend to be from the northwest or west, moving across the agricultural region and into the city of Lompoc (Johnson, 1998; Figures 2 and 3).

For the purposes of this study, the boundary of the pesticide-use area is 38.8 square miles (Figure 3) and consists of the Township-Range sections listed in Table 6. This list of sections was previously accepted by the LIWG as reasonable for defining the area of pesticide use that could potentially affect air in the city of Lompoc.

Air monitoring will be conducted at five sites located inside the city limits of Lompoc. Three of the five air sampling sites were selected to be representative of areas where the highest fumigant concentrations are hypothesized, based on proximity to fumigant application sites and predominant wind patterns during that time of year. The fourth site, near the center of Lompoc, was selected to be representative of fumigant concentrations that might be found closer to the center of the city. The fifth site is located in the northeast region of Lompoc to capture applications that might occur in the smaller agricultural areas to the north and east of the city.

Define the Temporal Boundary of the Decision Statement – In this project we will monitor for four fumigants during the winter (December through February), a relatively high use period for certain fumigants (Tables 3 and 4; DPR 1996, 1997a, and 1998) and a time of year when air inversions in the Lompoc valley are anticipated. Fumigant sampling may be extended into March and April and then occur again in the fall of the

year 2000, depending on the actual number of fumigations that occur during the above, predetermined study period. The extension of air sampling beyond February will be discussed with TAG members as the monitoring study progresses.

The Santa Barbara County Agriculture Commissioner's Office will notify DPR staff approximately 24 hours prior to every fumigant application. (See section 4.16 for the notification plan.) Air monitoring will begin within 24 hours of notification of DPR staff in order to capture the time that applications are scheduled to begin. For safety reasons, air sample changes will not be conducted at night because samplers are located on roofs and are accessed with ladders. These roofs have no safety rails. Therefore air sampling will be conducted for 8 hours during daylight (+/- one hour) and 16 hours at nighttime (+/- one hour).

Scale of Decision Making - Decisions will be based on air concentrations measured at the monitoring sites established in the city of Lompoc and on modeling results.

Identify Practical Constraints on Data Collection - There are several constraints on data collection:
1. The time of monitoring is constrained to one winter season, namely December 1999 through February 2000, for these four fumigants. Sampling is to be conducted during these months where historically certain fumigants have the highest use (Tables 3 and 4).

Mitigation of Constraint: The monitoring period may be extended to cover fumigant applications that occur in spring and fall of the year 2000. This will be discussed with members of the TAG. In addition, modeling will be conducted to simulate an application that might lead to higher air concentrations than the applications monitored during this season. (See section 7.5.)

2. With the exception of chloropicrin and methyl bromide, each fumigant will be monitored individually (not simultaneously) due to the limited supply of air sampling equipment (owned by the participating agencies) and required flow rates. (Note: fumigants are analyzed separately due to different requirements for air sampling tubes, flow rates, and/or analytical methods.)

Mitigation of Constraint: If two fumigants are applied within three days of one another, the application that is not monitored will be modeled to estimate expected ambient air concentrations within the city limits.

3. Sampling during winter periods does not necessarily ensure that maximum concentrations will be measured since air concentrations are dependent on factors other than use, including meteorological conditions, and location of applications relative to air samplers.

Mitigation of constraint: Modeling of an application closer to the city limits than those monitored, will be conducted to estimate potential exposures that may be higher than those measured in this study (see section 7.5).

4. Siting criteria for air sampler locations might prevent monitoring at locations of actual maximal concentration. The location of monitoring is constrained to the city of Lompoc and places within that which meet the U.S. EPA siting criteria (Appendix E). Sites not meeting these criteria may have higher concentrations.

Mitigation of constraint: Modeling of an application closer to the city limits than those monitored, will be conducted to estimate potential exposures that may be higher than those measured in this study (see section 7.5).

5. Due to monetary constraints, monitoring cannot be conducted on each day of the high use season, therefore days not monitored might have higher or lower concentrations.

Mitigation of constraint: Modeling of an application closer to the city limits than those monitored, will be conducted to estimate potential exposures that may be higher than those measured in this study (see section 7.5).

6. Concentrations will be measured during 8- and 16-hour periods. Some chemicals can cause effects during shorter duration exposures.

Mitigation of constraint: Modeling of an application closer to the city limits than those monitored, will be conducted to estimate potential exposures of a shorter duration (see section 7.5).

7. Due to monetary constraints, this study will only provide information on pesticide active ingredients except in the case of metam sodium, where only the primary breakdown product will be analyzed (see section 5.1). Also, data will not be gathered for inert ingredients, adjuvants, industrial chemicals, or other pesticide product components that could potentially affect human health. Certain breakdown products, adjuvants, inert ingredients, etc. might pose an equal or greater human health risk.

Mitigation of this constraint: There is no mitigation for this constraint. At this time there are no funds for monitoring of additional chemicals other than those proposed for phase two. Members of the TAG and/or LIWG may wish to re-direct money to monitor for additional chemicals.

8. Methyl bromide may have non-agricultural uses in the area (e.g., structural fumigations of residences) and may be produced from natural sources (e.g., the ocean).

There will be insufficient information to determine the relative contributions of each source to the overall air concentrations measured.

Mitigation of constraint: Concentrations of methyl bromide derived from oceanic sources will be included in the final report. This information will be collected from the existing scientific literature.

9. This study will only estimate inhalation exposure. Potential exposure to pesticides by ingestion, dermal absorption, or other potential routes will not be measured.

Mitigation of constraint: There is no mitigation planned for this constraint because for fumigants, the major route of exposure is expected to be through inhalation due to the high volatility of these chemicals.

10. Some concentrations may be too low to quantify given the current state of our technology for chemical analysis.

Mitigation of constraint: Data below the limit of quantitation will be set equal to the mid-point between the limit of quantitation and the method detection limit in mathematical calculations.

11. Three monitoring sites are located on the western edge of Lompoc in an effort to measure maximum concentrations. This placement does not guarantee that higher concentrations will not occur at other locations. Based on our knowledge of wind patterns and the location of agriculture relative to Lompoc, this was deemed the logical place to focus our sampling efforts.
(Note: The placement of samplers was discussed with and agreed to by members of the TAG in March 1999. In that meeting it was decided to use four sites, three on the west side and one closer to the center of Lompoc. Subsequently, the LIWG approved the plan (Appendix F). In October 1999, the issue of number of sites was re-visited by the TAG with agreement on October 26, 1999 to add the fifth site in the northeast region of Lompoc.)

Mitigation of constraint: Modeling of an application closer to the city limits than those monitored, will be conducted to estimate potential exposures that may be higher than those measured in this study (see section 7.5).

1.2.5 Develop a Decision Rule

Specify the Statistical Parameter that Characterizes the Population – For evaluating acute exposure to ambient air levels of individual fumigants monitored in this study, the parameter of interest will be the maximum 24-hour time-weighted average air

concentrations (averaged from sequential 8- and 16-hour concentrations) at any site during each fumigation.

Specify the Action Level for the Study – For the purposes of this study, the action levels will be the screening levels. Screening levels for acute exposures have been proposed by the DPR and subsequently reviewed by members of the TAG (Table 1 and Appendix B).

Develop a Decision Rule – If the maximum 24-hour time-weighted average air concentration is below the acute screening level, no immediate action will be taken (Table 1). However, DPR may still consider further analysis (e.g., additional modeling, further monitoring, and/or a more detailed analysis of the health effects data). If the maximum 24-hour time-weighted average air concentration is equal to or greater than the acute screening level then DPR will respond immediately with development of a plan for further analysis and/or interim regulatory action (Table 1). Regulatory actions could consist of one or more of the following: permit conditions for restricted materials (e.g., buffer zones), statewide regulations, label changes, suspension, and/or cancellation. The selection and implementation of any regulatory actions are outside the scope of this study.

The same decision rules apply to calculated concentrations made to estimate subchronic exposures (Table 1). (See section 7.1 for subchronic exposure calculations.)

1.2.6 Specify Limits on Decision Errors

Range of Concentration - Based on previous pesticide air monitoring in Lompoc and monitoring data from other studies, the possible range of concentrations for the fumigants is no detectable amount to 200 micrograms per cubic meter ($\mu g/m^3$; Kollman, 1995).

Identify the decision errors and choose the null hypothesis:
Define Both Types of Decision Errors and Establish the True State of Nature for Each Decision Error – There are two decision errors, i) deciding that the maximum 24-hour time-weighted average air concentration exceeds the screening level when it does not, and ii) deciding that the maximum 24-hour time-weighted average air concentration does not exceed the screening level when it does.

> The true state of nature for decision error (i) is that the maximum 24-hour time-weighted average air concentration does not exceed the screening level.
> The true state of nature for decision error (ii) is that the maximum 24-hour time-weighted average air concentration exceeds the screening level.

Specify and Evaluate the Potential Consequences of Each Decision Error - (i) If the 24-hour time-weighted average concentrations do not exceed the screening level, but

inadequate or incorrect data indicate that they do, DPR would mitigate the exposure without sufficient cause. This has implications for pest management, alternative pesticides, crop yields, and costs to growers and consumers. (ii) If the 24-hour time-weighted average concentrations do exceed the screening level, but inadequate or incorrect data indicate that they do not, a potential health hazard might not be mitigated.

Establish Which Decision Error has More Severe Consequences Near the Action Level - Decision error (ii) has the more severe consequences because an unmitigated health hazard outweighs the consequences of economic costs.

Define the Null Hypothesis (Baseline Condition) and the Alternative Hypothesis and Assign the Terms False Positive and False Negative to the Appropriate Decision Error - The baseline condition or null hypothesis is that the maximum 24-hour time-weighted average air concentration exceeds the screening level. The alternative hypothesis is that the maximum 24-hour time-weighted average air concentration is below the screening level.

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Specify a Range of Possible Values of the Parameter of Interest Where the Consequences of Decision are Relatively Minor (Gray Area) –

The screening levels all incorporate conservative uncertainty factors. Exceeding a screening level, therefore, does not mean than a health impact will in fact occur. It implies that the margin of safety built into the level is being eroded. The greater the exceedance, the closer the exposure will be to an adverse effect level. This occurs on a continuum, rather than at a specific point. This continuum can be described as a gray area. The gray area for MITC is the region between the acute screening level (6.6 $\mu g/m^3$) and about 50 $\mu g/m^3$. Within this region, there are not expected to be adverse health consequences of erroneously rejecting the null hypothesis.

Assign Probability Limits to the Points Above and Below the Gray Region that Reflects the Tolerable Probability for the Occurrence of Decision Errors –

The following limits are proposed for MITC (Figure 4). Below the gray region (below 6.6 $\mu g/m^3$), the tolerable probability of decision error is 10 % (i.e., there should be at least 90 % probability of rejecting the null hypothesis when the true maximum 24-hour time-weighted average is below the screening level). Above the gray region (50 $\mu g/m^3$), 10 % error is tolerable up to a true maximum 24-hour time-weighted average of 66 $\mu g/m^3$. Above 66 $\mu g/m^3$, only 1 % error probability is tolerable because significant health consequences would be more likely.

1.2.7 Optimize the Design for Obtaining Data

Review the Data Quality Objective Outputs and Existing Environmental Data - The TAG

will review the data quality objectives (DQOs) and Fumigant Sampling and Analysis Plan, in addition to the DQO outputs. Monitoring data from Phase One for MITC are viewed as estimates due to the length of time samples were stored prior to analysis. The expected concentrations may be greater than or equal to the values reported. The estimated maximum 12-hour concentration was 1 $\mu g/m^3$ of MITC. The estimated maximum 24-hour time-weighted average concentration was 0.75 $\mu g/m^3$. The coefficient of variation (CV) for 24-hour time-weighted averages was 209 %. Although the concentrations measured in Phase One are believed to have been biased downward due to poor quality control of the samples, this should not have affected the CV. This is because the distributions of concentration around each point on a first-order decay curve are lognormal, and while the variance decreases with the mean level, the CV remains constant. In earlier ambient monitoring of MITC in Kern County in July 1993, June 1997, July 1997 and January 1998, the maximum 12-hour concentrations found were 18, 9.2, 31 and 4.1 $\mu g/m^3$, respectively. The CVs were 121, 185, 188 and 98 percent (CARB, 1994; Seiber *et al*., 1999). Other monitoring data indicate air concentrations vary with numerous factors such as distance from the application, time after application, application rate, acreage, method of application, and meteorological conditions.

Alternative Data Collection Approaches - There are a number of possible approaches to data collection. Three of those approaches are outlined below, with a minimum of one strength and one limitation expressed for each.

Ambient Air Monitoring Approach –

One approach would be to conduct ambient air monitoring within the city of Lompoc. Air concentrations are considered an integral part of any study of the relationship between pesticide levels in air and community health effects. The strength of this approach is that air levels are measured, not estimated from a model. The limitation of this approach is that all possible combinations of pesticide use and meteorological conditions can not be approximated.

Application Site Monitoring-

Another alternative is to measure application site air concentrations and subsequently model the air concentrations projected for ambient air in the city of Lompoc. Application site monitoring would be used to back-calculate flux rates for each fumigant. This flux rate would then be incorporated into the model to then project ambient air concentrations within the city limits. The strength of this approach is that it would provide much needed information on various flux rates that might be expected from fumigant applications. The limitation of this approach is that it is more expensive than the other approaches. It also does not supply the desired information about measured air concentrations within the city limits. Air concentrations measured outside the city limits does not meet the stated goals and objectives of the plan nor does it conform to the desired study boundary conditions outlined above.

Combination of Ambient Air Monitoring and Modeling-
Another alternative is to combine ambient air monitoring within the city limits with modeling. Modeling would be used to supplement measured air concentrations in the event a large application, close to the city limits does not occur within the specified monitoring period. The strength of this approach is the flexibility afforded by modeling, providing information about air concentration estimates within the city limits given application scenarios that did not occur during the monitoring period. It also contains the desired element of measured ambient air concentrations within the city limits. One major limitation is the absence of measured flux rates from the Lompoc valley. Flux rates vary with soil type, condition and meteorological conditions. Maximum flux rates have been found to vary as much as 58% based on measured values for methyl bromide flux (Barry, 1995).

We have selected the combined approach, ambient air monitoring and modeling as the most cost effective approach that still meets our study objectives.

Develop General Data Collection Design Alternatives –
Simple Random Sampling -
For the present study, simple random sampling would involve choosing the sample locations by selecting points randomly in three spatial dimensions (i.e. latitude, longitude, and height), and choosing the sample starting times randomly within the study period.

Systematic Sampling -
Systematic sampling would involve choosing the sampling locations at evenly spaced distances in the three spatial dimensions, and choosing the sample times at evenly spaced intervals.

Stratified Random Sampling –
Stratified random sampling would divide the study area into distinct subareas with different, known probabilities of having the highest 24-hour concentration. Similarly, the study period would be divided into subperiods with different, known probabilities of having the highest 24-hour concentration. A predetermined proportion of the total samples would be randomly selected from each subarea/subperiod combination, with the proportion depending on the probability of highest concentrations in that combination.

Formulate the Mathematical Expressions Needed to Solve the Design Problem for Each Data Collection Design Alternative –
Because of the practical constraints on the location and scheduling of sampling events, none of the three design alternatives outlined can be implemented. Because it is desirable to maximize the probability of capturing peak concentrations, and because peaks are expected to be associated both spatially and temporally with fumigant applications, neither Simple Random Sampling nor Systematic Sampling would be very efficient.

Stratified Random Sampling would be preferred, if the data existed to define the strata. Since they do not, the sampling strategy that will be used is a qualitative approximation to Stratified Random Sampling. Existing monitoring data are not adequate to characterize statistically the spatial and temporal distribution of peak concentrations. Instead, the monitoring sites and times chosen are those expected to have the highest concentrations based on past fumigant application patterns and meteorological data.

Select the Optimal Sample Size that Satisfies the DQOs for Each Data Collection Design Alternative –
The study design is not statistically based, and therefore, no statistical methods for estimating precision or power are exactly applicable. Statistical methods for simple random sampling have been used to evaluate the planned study design, but the use of these methods must be considered as approximate, providing guidelines only.

Because only MITC has ambient monitoring data for the Lompoc area, the statistical calculations related to the design of the study have been done for MITC only. Metam-sodium is the most heavily used fumigant in the Lompoc area, and it is expected that most fumigant applications during the study period will be of metam-sodium. For the other fumigants, it is anticipated that all applications that occur in the study period will be monitored. The statistical power and error rates for the hypothesis tests will be calculated after the data are collected, and will be presented in the report.

The planned study design calls for a total of 150 samples (75 pairs consisting of one 8- and one 16-hour sample) for MITC (5 sites times 5 applications times 3 days per application). (See section 7.1 for the calculation of the 24-hour time-weighted average concentration.)

Previous ambient monitoring has not been coordinated with applications of fumigants, so the data do not contain relevant information about the magnitude of temporal and spatial variability. It is therefore not possible to determine a statistically optimal number of sites nor of applications to monitor. Given the historical information on the number of applications expected to occur in the study area, the study plan to monitor five applications per fumigant is likely to capture most applications. Nor is it possible, also due to the absence of data on inter-application variability, to determine an optimal number of samples per application. Instead, the sample size calculations are based on the total number of samples. That is, 5 applications times 3 days per application is treated as identical with 3 applications times 5 days per application. (Modeling that is to be done after the data are collected will help to address the questions of spatial and temporal variability.)

For acute effects, the null hypothesis is that the maximum 24-hour time-weighted average concentration is greater than or equal to 6.6 $\mu g/m^3$ (for MITC). The statistical test will be

to reject H_0 if the maximum 24-hour time-weighted average value is less than the acute screening level of 6.6 $\mu g/m^3$.

The power and error rates of the hypothesis were determined using computer simulation. Because ambient air concentrations typically have a lognormal distribution, and because the true maximum value in a lognormal distribution is undefined (being infinite), the distributions under possible alternate hypotheses were defined in terms of the population 99.98^{th} percentile. Assuming that 24-hr average concentrations from the pooled sites and fumigations have a lognormal distribution whose CV is 200% (from the CV in the 1998 monitoring data), and whose 99.98th percentile equals a given value *q*, the parameters μ and σ were found by solving the equations for the CV and 99.98th percentile of a lognormal distribution:

$CV = 2.0 = \sqrt{(\exp\{\sigma^2\} - 1)}$, and 99.98^{th} percentile = $q = \exp\{\mu + 3.54\sigma\}$.

The power of the test against alternate hypotheses was calculated by simulating 10,000 sets of 75 values from lognormal distributions with a CV of 200% and 99.98th percentiles equal to 4, 6.6, 10, 20, 30, 40, 50, 60,66 or 100 $\mu g/m^3$. Ten thousand sets of 75 samples from the parent population were simulated and the maximum value found in each set. In each set, the null hypothesis that the maximum 24-hour time-weighted average concentration is greater than or equal to the screening level was rejected if the maximum 24-hour time-weighted average concentration was less than 6.6 $\mu g/m^3$. The power of the test is the proportion of sets in which the null hypothesis was rejected (Figure 4).

Power of the test of H_0: Maximum 24-hour time-weighted average concentration $\geq$ 6.6 mg/m^3 against alternative hypotheses (n=75).

True value of 99.98th %ile ($\mu g/m^3$)	Power (prob{reject H_0})
100	.001
66	.024
60	.047
50	.108
40	.230
30	.437
20	.717
10	.945
6.6	.983

Select the Most Resource-Effective Data Collection Design that Satisfies All of the DQOs – Because the study design is dictated by practical constraints and data limitations, the non-statistically based site selection design was selected.

The power calculations indicate that if independent samples were randomly selected from the hypothetical lognormal population, 75 samples would be an adequate number. Because the independence and random sampling requirements cannot be met, however, these calculations can only be considered approximate.

Document the Operational Details and Theoretical Assumptions of the Selected Design in the Sampling and Analysis Plan – The chosen design is expected to give the highest probability of detecting the maximum 24-hour time-weighted average fumigant concentration within the city limits with the available resources. Three sampling sites will be established on the west side of Lompoc, closest to the agricultural area and where the highest concentrations are expected. One site will be located in the northwest corner of Lompoc, one on the center-west side, and one in the southwest corner (Figure 3). An additional site will be located near the central part of Lompoc, as recommended by the Air Resources Board and the U.S. EPA staff involved with this study. In addition, the

location of a sampling site on the eastern edge of town was raised for the TAG consideration. There have been fumigants applied to fields east of Lompoc. Therefore, in an effort to capture potential influx of fumigants from eastern applications, a fifth site is located in the northeast region of Lompoc. Members of the TAG will be asked to re-evaluate the addition of an air sampler on the eastern edge of town given a recent increase in methyl bromide fumigations on the east side.

Monitoring locations were selected to represent the portion of the city that would likely have the highest fumigant concentrations, given the location of applications and general wind patterns in the valley. Modeling potential fumigant concentrations in the city to help locate air-sampling locations was not conducted. The possibility of conducting this type of modeling was discussed with technical staff from the Air Resources Board, U.S. EPA, and DPR at a meeting held on Oct. 5, 1999 in Sacramento. It was decided by meeting participants not to model air concentrations to assist with site selection due to: 1. the uncertainty and variability in model-input data, 2. the amount of time required to make multiple model runs of even a small fraction of the potential application and wind pattern combinations, and 3. the inability for modeled outputs to pinpoint the one site expected to have the peak concentration.

Monitoring will occur during a high use period as indicated by pesticide use reports. The number of applications that will occur during this period is unknown; some fumigants may not be applied at all. Up to 13 applications will be monitored.

2. SITE DESCRIPTION

2.1 Topography

The city of Lompoc is a small city located in a coastal valley of Santa Barbara County, California (Figure 1). The population has been estimated at 37,649 in a U.S. Census conducted in 1990. The city is located approximately seven to eight miles east of the coastline. The valley is oriented roughly northwest to southeast and the surrounding hills form a V shape fanning out towards the ocean. Hills to the east of Lompoc tend to stall air movement as it passes the city, while the air is funneled eastward through the Santa Ynez River basin. Vandenberg Air Force Base (a rocket launch facility) and agricultural fields dominate the area between Lompoc and the coast. Five major crops or crop groups are grown in this area: cole crops (broccoli, cabbage, and cauliflower), lettuce, dried beans, celery, and flowers.

2.2 Climate

The region is dominated in summer months by a Pacific high-pressure area. This high-

pressure area tends to produce northwesterly winds in the Lompoc area. Aiding this tendency, the Central Valley of California heats up during the summer and creates a large pressure and temperature differential between inland and ocean surfaces. The air aloft from the Pacific high is generally warming and descending as it approaches the coastline near Vandenberg Air Force Base. Consequently, the cool moist marine area below tends to form a subsidence inversion accompanied by frequent fog or low cloudiness. The northwesterly winds exert pressure on the ocean surface that causes up-welling of cool water. This cools the air near the surface and contributes to fog formation. During winter, the Pacific high weakens, the jet stream shifts southward, and heating of the Central Valley is weaker or absent. Winds tend to be more westerly and frontal systems move through the area, changing the wind direction more frequently than in summer months. This summary and a complete description of weather patterns for Lompoc are given in Johnson, 1998.

2.3 Pesticide Use

The information given in this section was extracted from DPR's pesticide use report database. Data for 1996 and 1997 are complete and validated. As of December 1999, data for 1998 are complete, but not yet validated. Therefore, use report data from 1998 are considered preliminary and subject to change. A complete description of the pesticide use report database is given in DPR, 1995.

Between 1996 and 1998, approximately 120 pesticides have been used for agricultural production in the Lompoc area, with approximately 120,000 pounds used per year. Consistent with the crops and climate, insecticides and fungicides are the most heavily used pesticides in the Lompoc area. The pesticides used in the greatest amounts for agricultural production are shown in Table 1.

Fumigants are a unique class of pesticides. They are highly volatile, applied infrequently, but at higher rates than other pesticides (50 to 400 pounds per acre), and used to control a wide variety of pests and diseases. Between 1996 and 1998, there were 83 applications of the fumigant metam-sodium, ten of methyl bromide/chloropicrin, and one of 1,3-dichloropropene, compared to approximately 2000 for the insecticide chlorpyrifos (DPR 1996, 1997a, and 1998). However, the 94 fumigant applications accounted for almost 120,500 pounds of the 360,000 total pounds of pesticides. Fumigants are applied prior to planting. Therefore, many applications occur during the fall and winter (Tables 4 and 7). In the Lompoc area, most fumigants are injected below the soil surface and occasionally through drip irrigation systems. Because of their high volatility and high application rates, fumigants are the focus of the monitoring described here.

The Township, Range, and sections, plus patterns of fumigant use summarized for 1996 through 1998, are displayed in figures 5 through 9. The individual applications used to

summarize these figures are listed in Table 7.

3. PREVIOUS INVESTIGATIONS

3.1 Study of Hospital Discharges

An analysis of hospital discharge data from 1991-1994 suggests that certain respiratory illnesses occur in Lompoc at higher rates than in other comparison areas. The State's Office of Environmental Health Hazard Assessment evaluated these data (Wisniewski et al., 1998; Ames and Wisniewski, 1999). The evaluation indicated that the proportion of hospitalizations due to respiratory illnesses, in particular bronchitis and asthma, were elevated in Lompoc relative to the proportion of hospitalizations in the comparison areas, with some differences by age. The incidence of lung and bronchus cancers also was increased above the expected numbers based on regional rates. The purpose of the report was not to speculate on the cause of the illnesses; rather, it was to evaluate the incidence of specific illnesses.

3.2 Phase One of Pesticide Air Monitoring

The Phase One study was intended to test pesticide sampling and analysis methods and to determine if a subset of the total pesticides in use in the area could be measured in air. With some exceptions, these goals were achieved. The study was most successful in developing and demonstrating the multiple-pesticide sampling and analysis method. Due to the limited nature of the Phase One sampling, these results are not appropriate for risk assessment.

Over 50 pesticides were used in or near Lompoc during the August-September 1998 monitoring period. Air monitoring was conducted for twelve pesticides with recorded use in those months in prior years. Of the 12, five were not applied during the 1998 monitoring period, and were not detected in air samples. The remaining seven were detected in air samples. Many of these detected concentrations were between the sample detection limit and quantitation limit meaning that the existence of the pesticide in a sample, while likely, was too low to be assigned a numerical value. For example, chlorpyrifos, the most frequently detected pesticide, was detected in 55 of 119 samples above the quantitation limit of 4 ng/m^3, and in an additional 60 of 119 samples between the quantitation limit and the detection limit of 1 ng/m^3.

The results for MITC (the biologically-active breakdown product of metam-sodium) are estimates due to poor quality assurance/quality control of the samples. Qualitatively, the results may represent an underestimate of the MITC actually present in the samples. The highest concentrations of MITC were the result of one application of 720 pounds of

metam-sodium on 7.5 acres approximately one mile west of Lompoc.

Cycloate was not one of the 12 pesticides on the monitoring list, but was detected during laboratory screening. Concentrations of cycloate are considered to be estimates because of limited laboratory quality assurance.

The metal analyses were originally intended as surrogates for pesticides containing metals (aluminum in fosetyl-Al, and manganese in maneb and mancozeb). In retrospect, these analyses are not capable of discriminating between pesticide-applied sources and natural background sources, e.g., soils. Results should not be interpreted as indicative of the presence or absence of these metal-containing pesticides in air.

Silicon was tested for and found in Lompoc air during the monitoring period. Levels were found as high as 17 $\mu g/m^3$, close to the highest level measured in California urban areas during recent years.

3.3 Air Concentrations of Fumigants Measured in California

Air sampling was conducted by the Air Resources Board, in consultation with DPR for a variety of pesticides in accordance with the Toxics Air Contaminant (TAC) monitoring program. Monitoring for pesticides is conducted in counties with the highest use for a particular pesticide to be monitored and during the season of highest use. The following summarizes information from air sampling conducted under the TAC program.

1,3-Dichloropropene was measured in Merced County in April 1990 using coconut-based charcoal sorbent and analyzed by gas chromatography and an electron capture detector (Baker et al., 1996). Four sites were measured over the course of eight days and all concentrations were above the minimum quantitation level of 0.10 $\mu g/m^3$. The maximum concentration was 160 $\mu g/m^3$, the average was 24 $\mu g/m^3$, and the mean urban background concentration was 0.90 $\mu g/m^3$.

Chloropicrin was measured in Monterey County in September 1986 using XAD-4 resin and analyzed by gas chromatography and an electrolytic conductivity detector (Baker et al., 1996). Three sites were measured over the course of 16 days with 28% of the samples above the minimum quantitation level of 0.085 $\mu g/m^3$. The maximum concentration was 4.6 $\mu g/m^3$, the average was 0.64 $\mu g/m^3$, and the mean urban background concentration was <0.085 $\mu g/m^3$.

MITC was measured in Kern County in July 1993 using coconut-based charcoal sorbent and analyzed by gas chromatography and a nitrogen-phosphorous detector (Baker et al., 1996). Four sites were measured over the course of eight days with 83% of the samples

above the minimum quantitation level of 0.01 $\mu g/m^3$. The maximum concentration was 18 $\mu g/m^3$, the average was 5.8 $\mu g/m^3$, and the mean urban background concentration was 2.1 $\mu g/m^3$.

Methyl bromide was measured in Monterey County in September 1986 using petroleum-based sorbent and analyzed by gas chromatography and an electron capture detector (Baker et al., 1996). Three sites were measured over the course of 16 days with 1% of the samples above the minimum quantitation level of 4.2 $\mu g/m^3$. The maximum concentration was 4.4 $\mu g/m^3$, the average was 4.1 $\mu g/m^3$, and the mean urban background concentration was <4.2 $\mu g/m^3$.

4. SAMPLE COLLECTION DESIGN

The design for sample collection is a product of the DQO process as well as a result of community and technical input from the TAG and LIWG. This section describes the types of samples to be collected, sample measurement details, numbers of sampling sites and their general location, and other information pertinent to field collection and shipment of samples.

4.1 Safety

Sampling of air in the city of Lompoc does not pose an occupational hazard for the sampling crew. However, a concern exists for sampling crew safety. Air samplers are located on rooftops for sample security purposes and access to the roofs is by ladder. Due to the lack of safety guardrails on the rooftops, air sample changes will be restricted to daylight hours. Sunrise on the shortest day of the year in December is approximately 7:05 A.M. and sunset is approximately 4:55 P.M. In addition, it takes approximately two hours to change the tubes at five sites. For that reason, air sample changes during this study will be conducted at a mean time of 8:00 A.M. and 4:00 P.M. Therefore, field staff will commence daylight sampling at the first site at 7:00 A.M. and finish roughly at 9:00 A.M. and commence nighttime sampling at 3:00 P.M. and finish roughly at 5:00 P.M.

An additional safety consideration is sampling during rainfall events. Due to slick surface conditions on rooftops and the lack of guardrails, sampling will not be conducted when it rains. In the event of a light rain or drizzle, field-sampling staff will proceed with sampling if they are confident it is safe to do so.

4.2 Sampling Theory

In Phase One sampling, five sites were used to monitor air concentrations in Lompoc

(Figure 1). In discussion with the TAG on October 26, 1999, a sampling plan was formulated based on study objectives and monetary constraints. The TAG decided to monitor the original five sites. The sites of primary concern were those along the western edge of the city due to proximity to the majority of the agriculture in the valley and the predominance of wind directions from the west and northwest. During the months of November through January, the winds are from the west and northwest just over 50% of the time (Figure 2). The group decided to coordinate sampling with specific applications that occur in the valley, meaning when an application occurs, monitoring will begin. Based on historical information from flux of each of the fumigants, the highest concentrations measured around treated fields tend to occur within three days of application (ARB, 1987; Ross et al., 1996; Beard, 1994; Fitzell, 1993). Therefore, the TAG recommended three days of monitoring in an attempt to capture peak air concentrations which residents in Lompoc might be exposed. Due to historical problems with breakthrough of some of the fumigants at long sampling intervals (greater than 12 hours), two samples will be collected during a single 24-hour period to equate with the 24-hour screening level. In addition, flow rates were lowered to prevent breakthrough, yet not lowered too much so as to compromise the desired detection limits. In addition to lowering the flow rate, breakthrough problems with methyl bromide were alleviated by adding a secondary tube to the sampling train. Both the secondary and primary tubes will be analyzed.

For each fumigation event, a minimum of 30 samples (60 for methyl bromide) will be collected (two samples per day x three days x five sites, and four samples per day x three days x five sites for methyl bromide). Add to this two duplicates (four for methyl bromide), two trip spikes (four for methyl bromide), two trip blanks, and three field spikes (6 for methyl bromide), yields 39 samples (76 for methyl bromide) per fumigation event for the primary laboratory. This does not include any continuing quality control samples run in the laboratory or blank sample tubes held in the laboratory for analysis with incoming field samples. The TAG requested that as many fumigation events as possible be sampled.

At its March 19, 1999 meeting, the TAG and LIWG agreed to the following budget for fumigant monitoring:

Primary laboratory analysis	$60,000
Quality Control	6,000
Second laboratory	6,000
Field sampling	10,000
Mini-Sodar met station	16,000
Miscellaneous costs	2,000

At its October 26, 1999 conference call, the TAG agreed to the following revised budget:

Primary laboratory analysis	$80,000
Quality Control	included in cost of primary lab
Second laboratory	provided at no charge by DPR and EPA
Field sampling	20,000
Mini-Sodar met station	redirected to sampling and analysis
Miscellaneous costs	0

The field and laboratory contracts charge personnel and operating expenses against this budget, as opposed to per sample charges. Method development and validation by the primary laboratory cost approximately $40,000 (Appendix D). Each application monitored costs between $1500 - $2000 for field sampling and $3000 - $4000 for laboratory analysis (Appendix D). Between 10 and 13 fumigant applications can be monitored with the available funds.

The distribution of the number of fumigations to be monitored for each fumigant was based on the historical number of applications made for each fumigant (Tables 3, 4 and 7). Therefore, the minimum numbers of fumigations to be monitored: one for 1,3-dichloropropene, two for chloropicrin, five for metam sodium, and two for methyl bromide. This adds to 10 fumigation events. (Note, chloropicrin and methyl bromide are combined in the formulated products used in Lompoc, but have to be analyzed separately due to differences in sampling and analytical measurement requirements. However, they will be monitored together since we have flow splitters that attach to each air sampler and can accommodate to two different air-flow rates. Other fumigants cannot be measured simultaneously because of the limitations of our sampling equipment.) The TAG will meet to determine which additional fumigations should be monitored.

Statistical power calculations (see Section 1.2.7) indicated that if the samples were randomly selected from a lognormal population, 75 24-hour time-weighted average concentrations per fumigant would be an adequate number for testing the null hypothesis. They further indicated that little power is gained by increasing the number of samples. Because the random sampling requirement cannot be met, however, these calculations can only be considered approximate.

The DPR statistician will estimate the number of samples needed for the remaining fumigants prior to monitoring for those fumigants.

4.3 Sampling Method

This section will describe two field-sampling methods that will be used to measure air concentrations of the four fumigants. The first method uses sorbent tubes to trap the fumigants and sampling and chemical analytical methods have been established for all

four fumigants. The second sampling method uses canisters to trap air followed by chemical analysis of the gas inside the canister. Currently, methods using canisters are available for two of the four fumigants.

4.3.1 *Sorbent Tubes*

The most widely used procedure for atmospheric measurement of pesticides is to pass 2 to 100 liters of air per minute through a solid sorbent material onto which the pesticide is adsorbed (Keith, 1988). Sorbent media typically used to trap pesticides include XAD resins and carbon sorbents such as charcoal (Majewski and Capel, 1995; Keith, 1988; Baker, et al., 1996). In addition, lower flow rates (< one L/min) have been used to trap pesticides and prevent breakthrough on sorbent media during air sampling (Ross et al., 1996; Kollman, 1995).

4.3.2 *Canisters*

Canisters have been used as an alternative to solid sorbents for air sampling (Keith 1988). In addition, a study by Biermann and Barry (1999) indicated that methyl bromide recovery from canisters was significantly higher than recovery from charcoal sorbent tubes. For this reason, U.S. EPA staff recommended use of canisters for all fumigants to be monitored in this study. However, at this time, chemical analytical methods using canisters as the air sampling method are available for only two of the four fumigants (1,3-dichloropropene and methyl bromide). A third method for MITC is under development at the primary laboratory and might be completed by the end of February 1999. A method for chloropicrin is not available at this time.

4.4 Sample Type

Air samples will be run for consecutive 8- and 16-hour intervals during the course of a 24-hour period. For safety reasons, the change of air sampling tubes and canisters will occur in daylight hours. The 8-hour daytime sample will commence at 7:00 A.M. at the first site. The 16-hour nighttime sample will commence at 3:00 P.M. at the first site. This sequence of air sampling tube changes will continue until three days have been completed (72 hours of sampling).

4.5 Media

In addition to air samples, meteorological measurements of wind speed, wind direction, temperature, and relative humidity will be made. See section 4.13 for meteorological sampling details.

4.6 Collection Schedule

Certain pesticides are designated restricted materials. One of the requirements for use of restricted materials is that the county department of agriculture be informed by the applicator prior to application. All of the fumigants that will be monitored are restricted materials. The Santa Barbara County Department of Agriculture will inform sampling personnel when a fumigant application is scheduled for the Lompoc area, as defined by the agricultural region outlined in Figure 3. For each fumigation event, sampling will commence within 24 hours of notification by the Agricultural Commissioner's Office that an application will occur. For example, if field-sampling staff receive notice on Tuesday that an application will occur on Wednesday during the daytime, field sampling will begin at 7:00 A.M. on Wednesday. If field-sampling staff receive notice on Saturday that an application will occur Sunday night, monitoring will commence Sunday at 3:00 P.M. In summary, monitoring will commence with the daytime or nighttime period during which the application is scheduled to occur.

A maximum of 13 fumigant applications will be monitored. A minimum of 10 fumigations will be monitored: one 1,3-dichloropropene, two chloropicrin, two methyl bromide (note: chloropicrin and methyl bromide are applied together and will be monitored together), and five metam-sodium applications. As fumigations proceed, members of the TAG will be consulted concerning which additional fumigant applications to monitor. A minimum of 10 fumigant applications will be monitored as they occur from December 1999 through February 2000. Metam sodium fumigations of less than or equal to 150 pounds active ingredient, will not be monitored. Fumigations greater than 150 pounds active ingredient, will be monitored until the five fumigations are sampled. There are no pound limits for the other fumigants. The possibility of extending monitoring into April 2000, with another period of monitoring in the fall of 2000 is being explored with TAG members and laboratory and field contractors. For each fumigant application monitored, six sequential samples will be collected at each site, as described in 4.3 above. A schedule for sample collection is in Appendix G.

4.6.1 *Schedule for Quality Control Field Sampling*

In addition to field samples collected during a fumigation event, two to three duplicate (co-located) samples, three fortified spikes, four trip spikes, three trip blanks, and three confirmation samples will be collected.

A duplicate sample is a sample that is collocated with a field sample. The primary laboratory will analyze both duplicate samples. These samples serve to evaluate overall variation in sample measurement and analysis. Two duplicate samples will be analyzed for MITC, three duplicate samples will be analyzed for the remaining fumigants.

A fortified spike (also called a sample spike) is a laboratory spike prepared as soon as the primary laboratory is notified of a fumigation. This spike is then sent to the field and placed on an air sampler with air flowing through the sorbent tube. Once shipped to the field, it is treated just like a field sample, including storage and shipping conditions. The fortified spike, in comparison with trip spikes and the respective field sample, gives us some information about any change in our ability to recover the analyte during air sampling.

Four trip spikes will be generated in the primary laboratory, two at a high concentration and two at a low concentration within the range of concentrations anticipated. Trip spikes mailed to the field technician will be stored on dry ice until all samples for the single fumigation event are collected. Two of the four trip spikes, one high and one low, will be sent back to the primary laboratory with the field samples for analysis. The remaining two trip spikes will be mailed to the confirmation laboratory along with the confirmation samples (see below).

The tubes used for trip blanks will originate in the field. These tubes will be taken from the same storage shed where all other sampling tubes are kept prior to use. Two trip blanks will be mailed with the field samples to the primary laboratory for analysis. In addition, one trip blank will be mailed to the confirmation laboratory along with their respective samples.

A confirmation sample is a sample that is collocated with a field sample, yet analyzed by the confirmation laboratory. Three confirmation samples will be shipped with the two trip spikes and one blank sample to the confirmation laboratory for analysis.

The site and time of duplicate sampling, fortified sampling, and confirmation sampling was randomly assigned. The schedule for such sampling, as well as field sampling is located in Appendix G.

The number of trip spikes, blanks, and confirmation samples for canisters will follow similar procedures described above for sorbent tubes. The only limitation is the total number of canisters available. The number of trip spikes, blanks, and confirmation samples will be discussed with the laboratories and amended to this sampling plan.

4.7 Sampling Site Locations

Monitoring will occur at five sites within the city of Lompoc, one each in the northwest, central-west, southwest, northeast, and near the center of Lompoc (Figure 3). These sites were also used for Phase One. All locations meet the U.S. EPA siting criteria for ambient air monitoring sites (Appendix E). Samplers at all locations are on rooftops to ensure the security of the samples. As an extra measure of security, members of the TAG requested

that the exact street address of these sites not be included in sampling-plan documents.

4.8 Preparation for Sampling

Sample labels with the study number and sample identification number will be attached to all sampling tubes and canisters before delivery to field sampling staff. Chain of custody forms, sample analysis request forms, and a data log book will be supplied to field sampling staff. Samplers will be pre-calibrated in the laboratory for the flow rates required for air sampling. Permission for access to sampling sites has been confirmed at all five locations. A storage unit will be rented to house equipment and samples temporarily stored on dry ice. All equipment necessary for monitoring will be delivered to Lompoc and set-up prior to fumigation monitoring. Fumigation monitoring will not begin until formal approval for such activity is received from US EPA.

A MetOne® meteorological station will be placed approximately one mile west of Lompoc (Figure 1). The station will be operational prior to the start of monitoring. Meteorological data will be collected during the course of the entire monitoring period (December through February, and longer if sampling continues beyond February).

4.9 Equipment

Equipment to be delivered to field sampling staff

Record book
Data Log Book
SKC INC. personal samplers
AC adapters
Sampler support system
Rotameters
Flow Calibrators
Sample tubes; XAD-4 tubes, petroleum charcoal tubes, coconut charcoal tubes
Chain of custody forms
Request for analysis forms
Caps for tubes
Security Seals
Connectors for tubes
Tube breakers
MetOne® meteorological station
Campbell Scientific micrologger and storage modules
Compass
Allen wrenches
Spanner wrench

Anemometer
Sling psychrometer
Hand-held Thermometer
HobobTemp Temperature Data loggers
Ice chests or freeze-safes
Duct tape
Dry ice (to be purchased as needed)

Additional AC adapters are on order but all other equipment is available and operational.

4.10 Field Tests

Prior to field sampling, a trial run with fortified samples will be conducted. The primary laboratory will generate a minimum of four spikes and sent overnight mail, to DPR staff. A minimum of two samples will be run on air samplers for 16 hours. The samples will be shipped within 12 hours of sample collection, overnight mail, back to the primary laboratory. This trial run will be conducted to test shipping procedures, fortified spike procedures, accuracy of paperwork completion, and trapping efficiency of sorbent tubes.

In addition to the above trial run, a field test run will be performed to identify potential problems with the sampling procedures. The field technician will run through the entire procedure involved with one sampling interval, from sample placement through sample removal, temporary storage, and shipping to the appropriate laboratories. If approved by U.S. EPA, samples collected during this trial run will also be analyzed as background samples. The analyte for background sampling will be MITC.

The MetOne® meteorological station will be checked once a month against hand-held sensors (Appendix H). Storage modules will be exchanged and downloaded approximately once a month.

Air sampling pumps will be calibrated in the laboratory prior to monitoring. In addition, flow rates will be checked in the field before and after each sampling interval with a rotameter (Appendix H). Rotameters are checked against a flow calibrator in the laboratory.

4.11 Field Testing Procedure References

The use, operation, calibration and maintenance of air sampling pumps are described in DPR's SOP EQAI001.00 (Appendix H). Preparation of sorbent tubes for use with air sampling pumps is described in DPR's SOP FSAI001.00 (Appendix H). Preparation and usage of temperature data loggers that are placed in ice chests to record temporary storage and transport temperatures are described in DPR's SOP EQOT001.01 (Appendix

H). The meteorological station will be set up according to DPR's SOP EQWE001.00 (Appendix H).

4.12 Sample Collection References

Sorbent tube samples will be collected according to procedures listed in DPR SOP EQAI001.00 (Appendix H). Canister air samples will be collected according to US EPA Method TO-15 (US EPA, 1997). Instructions for field sampling personnel are detailed in DPR's protocol for air monitoring in Lompoc (Appendix G). Chain of custody forms, log book sample form, laboratory analysis request form, canister sampling data sheet and canister check-in sheet are appendices in DPR's air monitoring protocol (Appendix G). Canister cleaning methods (US EPA region 9 SOP #312) can be found in Appendix H.

4.13 Shipment of Samples

Samples will be shipped via UPS overnight. The samples will be packaged and shipped according to procedures in DPR's SOP QAQC004.1 (Appendix H). Each shipment of samples will be accompanied by a temperature data-logger to record sample temperatures from collection to delivery to the lab. Shipment of samples will be scheduled as soon as possible after final sample collection for each fumigation event. Sample shipment should be timed such that samples will not arrive in the laboratory on a weekend or holiday.

4.14 Meteorological Sampling

A MetOne® meteorological station will be set up at a site near the agricultural areas on the west side of the city of Lompoc. The station will be set up according to DPR's SOP EQWE001.00 (Appendix H). The MetOne® meteorological sensors will be placed on a trailer mast at a height of 10 meters. The sensors will record wind direction, horizontal wind speed, temperature, and relative humidity. The MetOne® sensors were calibrated by the manufacturer on October 5, 1999 to fit within the specifications of the manufacturer. The meteorological data will be recorded on a Campbell Scientific CR 21X Datalogger every 15 minutes as per U.S. EPA Guidelines on air quality models (revised), (see Appendix W of 40 CFR part 51 EPA-450/2-78-027R).

4.15 Pesticide Use Data

Pesticide use data will be collected from pesticide use reports submitted by growers to the County Agriculture Commissioner's Office. Universal use reporting, required by the state of California, directs all growers to submit details of pesticide usage on a monthly basis. California and New York are the only states in the United States that require such records.

As part of general enforcement procedures, staff from the Agriculture Commissioner's Office are required by law to perform inspections of 5% of all sites identified in permits or notices of intent to apply a pesticide for an agricultural purpose (3 CCR 6436). These inspections are performed on a non-appointment basis and cover various aspects of pesticide use such as compliance with permit and label requirements, application equipment inspections, mix/load inspections, and field-worker safety inspections. Department of Pesticide Regulation manual (DPR 1997b) details procedures that enforcement staff use to assure grower compliance with pesticide labels and state and federal laws regarding pesticide use.

Additional procedures for this study will include verification of the date, time, and location (Township-Range-section) of fumigant application by the Agriculture Commissioner's staff. Verification will be performed either by phone or site visit. Staff at DPR will verify with the Agriculture Commissioner's staff the date and time of the fumigation within 24 hours of the scheduled application.

4.16 Notification Plan

Upon receipt of the Notice of Intent (NOI) to apply any of the fumigants to be monitored, the district biologist for the Santa Barbara County Agricultural Commissioner's Office will call Lisa Ross on her cell phone. If the Commissioner's Office cannot reach Lisa, they will call Randy Segawa on his cell phone. Lisa (or Randy) will then call the field technician on his home/office phone. If the technician cannot be reached at that phone number, he will be paged on his pager. If the technician cannot be reached, we will attempt to send a field technician from DPR to Lompoc to ensure sampling begins with the appropriate sampling interval. The DPR technician is trained in the use of air sampling equipment used for this study. In addition, Lisa (or Randy) will phone and/or page the primary laboratory to notify them when sampling will begin and for which fumigant. All persons involved have phone message systems or voice mail in case other communication systems fail.

There may be occasions where an application will not be monitored, in spite of all the back-up procedures described above. In those cases, the Industrial Source Complex Short Term model (U.S. EPA, 1995) will be used to estimate concentrations that would have resulted from such an application.

5. SAMPLE ANALYSIS DESIGN

5.1 Constituents of Interest

The constituents of interest are the fumigants 1,3-dichloropropene, chloropicrin, and

methyl bromide. In addition, the biologically active breakdown product of metam sodium, MITC will be measured due to the short half-life of metam sodium and its low volatility (Table 8). MITC is the biologically active product for soil fumigations. Field research has demonstrated that 87% to 95% of the applied metam sodium degrades to MITC in various soils tested (Smelt et al., 1989; Burnett and Tambling, 1986; Gerstl et al., 1977; Leistra et al., 1974; Leistra, 1974; Smelt and Leistra, 1974; Turner and Corden, 1963). The conversion exhibited a half-life of less than 30 minutes to seven hours, and varied with soil conditions. Certain degradation products have been theorized or actually measured in air (Wales, 1999; Moilanen et al., 1978; Woodrow et al., 1983; Carter et al., 1997, Table 7). However, due to budgetary constraints, air measurement of additional atmospheric constituents cannot be addressed in this study.

5.2 Sample Preparation References

Chemical extraction methods for 1,3-dichloropropence and methyl bromide from sorbent tubes and removal from canisters are referenced below for the primary and confirmation laboratories. Chemical extraction methods for chloropicrin and MITC from sorbent tubes are referenced below for the primary and confirmation laboratories. (Note: At the time of this writing there were no analytical methods for chloropicrin and MITC sampled using canisters.)

5.2.1 *Chemical extraction methods for 1,3-dichloropropene from sorbent tubes*

The primary laboratory- Extraction for 1,3-dichloropropene from sorbent tubes will be performed in accordance with the SOP in Appendix I.
The confirmation laboratory- Extraction for 1,3-dichloropropene from sorbent tubes will be performed in accordance with the SOP in Appendix J.

5.2.2 *Removal of 1,3-dichloropropene from canisters*

The primary laboratory- An aliquot of air is removed from the canisters as described in the SOP in Appendix K.
The confirmation laboratory- An aliquot of air is removed from the canisters as described in the SOP in Appendix K.

5.2.3 *Chemical extraction methods for chloropicrin from sorbent tubes*

The primary laboratory- Extraction for chloropicrin from sorbent tubes will be performed in accordance with the SOP in Appendix L.
The confirmation laboratory- Extraction for chloropicrin from sorbent tubes will be performed in accordance with the SOP in Appendix M.

5.2.4 *Chemical extraction methods for MITC from sorbent tubes*

The primary laboratory- Extraction for MITC from sorbent tubes will be performed in accordance with the SOP in Appendix N.
The confirmation laboratory- Extraction for MITC from sorbent tubes will be performed in accordance with the SOP in Appendix O.

5.2.5 *Chemical extraction methods for methyl bromide from sorbent tubes*

The primary laboratory- Extraction for methyl bromide from sorbent tubes will be performed in accordance with the SOP in Appendix P.
The confirmation laboratory- Extraction for methyl bromide from sorbent tubes will be performed in accordance with the SOP in Appendix Q.

5.2.6 *Removal of methyl bromide from canisters*

The primary laboratory- An aliquot of air is removed from the canisters as described in the SOP in Appendix K.
The confirmation laboratory- An aliquot of air is removed from the canisters as described in the SOP in Appendix K.

5.3 Analysis Procedure References

Chemical analytical methods for 1,3-dichloropropence and methyl bromide from sorbent tubes and canisters are referenced below for the primary and confirmation laboratories. Chemical analytical methods for chloropicrin and MITC from sorbent tubes are referenced below for the primary and confirmation laboratories. (Note: At the time of this writing there were no analytical methods for chloropicrin or MITC trapped in canisters.)

5.3.1 *Chemical analytical methods for 1,3-dichloropropene extracted from sorbent tubes*

The primary laboratory- Analytical methods for 1,3-dichloropropene extracted from sorbent tubes will be performed in accordance with the SOP in Appendix I.
The confirmation laboratory- Analytical methods for 1,3-dichloropropene extracted from sorbent tubes will be performed in accordance with the SOP in Appendix J.

5.3.2 *Chemical analytical methods for 1,3-dichloropropene removed from canisters*

The primary laboratory- Analytical methods for 1,3-dichloropropene removed from canisters will be performed in accordance with the SOP in Appendix K.

The confirmation laboratory- Analytical methods for 1,3-dichloropropene removed from canisters will be performed in accordance with the SOP in Appendix K.

Request for analysis by the U.S. EPA region 9 laboratory will be requested prior to sampling using the form provided by U.S. EPA. Appendix K contains the form to be submitted.

5.3.3 *Chemical analytical methods for chloropicrin extracted from sorbent tubes*

The primary laboratory- Analytical methods for chloropicrin extracted from sorbent tubes will be performed in accordance with the SOP in Appendix L.
The confirmation laboratory- Analytical methods for chloropicrin extracted from sorbent tubes will be performed in accordance with the SOP in Appendix M.

5.3.4 *Chemical analytical methods for MITC from sorbent tubes*

The primary laboratory- Analytical methods for MITC extracted from sorbent tubes will be performed in accordance with the SOP in Appendix N.
The confirmation laboratory- Analytical methods for MITC extracted from sorbent tubes will be performed in accordance with the SOP in Appendix O.

5.3.5 *Chemical analytical methods for methyl bromide extracted from sorbent tubes*

The primary laboratory- Analytical methods for methyl bromide extracted from sorbent tubes will be performed in accordance with the SOP in Appendix P.
The confirmation laboratory- Analytical methods for methyl bromide extracted from sorbent tubes will be performed in accordance with the SOP in Appendix Q.

5.3.6 *Chemical analtyical methods for methyl bromide removed from canisters*

The primary laboratory- Analytical methods for methyl bromide removed from canisters will be performed in accordance with the SOP in Appendix K.
The confirmation laboratory- Analytical methods for methyl bromide removed from canisters will be performed in accordance with the SOP in Appendix K.

5.4 Initial Quality Control Requirements

Initial quality control consists of a standards check, verification of calibration, the method detection limit determination, and analysis of matrix spikes.

5.4.1 *Standards Check*

Each laboratory uses certified standards. The primary and quality control laboratories will exchange standards for each analyte for verification. The primary and quality control laboratories will also exchange standards at the end of the study. New standards are prepared at least every six months. New standards are compared with old standards for verification. Standards for fumigants have shown no degradation over a six-month period in prior studies.

5.4.2 *Verification of Calibration*

Both the primary and quality control laboratories verify calibration by analyzing a series of standards (samples containing known amounts of analyte dissolved in a solvent for the sorbent samples or air for the canister samples). The linear range of calibration is determined by analyzing standards of increasing concentration. Within the linear range, the calibration is determined by regressing the standard concentration on the response of the instrument (peak height or peak area of the chromatogram) using at least five concentrations. The minimum acceptable correlation coefficient of the calibration is given in the SOP for each method, but in general is at least 0.95. The calibration is verified with each set of samples analyzed as described in section 6.4 for continuing quality control.

5.4.3 *Method Detection Limit and Limit of Quantitation*

Each laboratory determined the method detection limit for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. This standard is analyzed at least seven times, and the method detection limit is determined by calculating the 99% confidence interval of the mean. This procedure is described in detail in U.S. EPA (1990). The method detection limit for each analyte and method is given in the SOPs.

The limit of quantitation is set a certain factor above the method detection limit. This factor is determined by the level of interference found in the samples. The more interference, the higher the factor. The limit of quantitation for each analyte, along with a summary of chemical analytical and air sampling methods, can be found in Table 5.

5.4.4 *Analysis of Matrix Spikes*

A series of matrix spikes (sorbent tube samples containing known amounts of analyte) were analyzed to determine the precision and accuracy of the methods. Each laboratory analyzed at least ten matrix spikes at various concentrations. The mean recovery and standard deviation were calculated for each method. Data for the matrix spikes are given

in the SOP for each method. The precision and accuracy are verified with each set of samples analyzed as described in section 6.4 for continuing quality control.

5.5 Laboratories

The primary laboratory for all four analytes, for all methods of sample collection, is the California Department of Health Services, Environmental Health Laboratory located at 2151 Berkeley Way, Berkeley, California 94704. The confirmation laboratory for all four analytes trapped with sorbent tubes is the California Department of Food and Agriculture, Center for Analytical Chemistry located at 3292 Meadowview Road, Sacramento, California 95832. The confirmation laboratory for all analytes trapped using canisters (i.e., 1,3-dichloropropene and methyl bromide, only) is the U.S. EPA, Region 9 Laboratory located at 1337 S. 46th Street, Building 201, Richmond, California 94804.

5.6 Sample Transit Conditions

Immediately following sample collection, all air samples collected using sorbent tubes will be placed in a cooler or freeze safe containing ample quantities of dry ice (see section 4.12 for details of sample shipment conditions). Upon arrival in the analytical laboratories and after sample check-in procedures, samples will be placed in secure freezers kept at -4°C or below. Canisters do not require special temperature conditions during sample handling or shipment.

5.7 Holding Times

Sample holding times were determined for each analyte using storage stability measurements performed in the laboratory. Sample holding time for 1,3-dichloropropene is 22 days (Table 5 and see Appendix I for data on storage stability). Sample holding time for chloropicrin is 42 days (see Appendix L for data on storage stability). Sample holding time for MITC is 14 days (see Appendix N for data on storage stability). Sample holding time for methyl bromide is 14 days (Biermann and Barry, 1999). Sample holding time for all fumigants trapped with canisters is 30 days (see Appendix K). This holding time begins at the time of sample collection to the time of extraction.

5.8 Trapping Efficiency

The trapping efficiency for each fumigant trapped on sorbent tubes is listed in Table 5.

6. DATA VALIDATION/QUALITY ASSURANCE

6.1 Sample Receipt Verification

Sample receipt, log-in, and verification procedures for each laboratory are in Appendix R.

6.2 Holding Time Verification

Holding times will be verified by date of sample collection and date of extraction listed on the chain of custody records and laboratory reports. Verification will be ensured in the laboratory by the lead chemist assigned to the project and also checked by the project leader at DPR.

6.3 Audit Results

The quality assurance (QA) team for this project, led by staff from the California Air Resources Board, submitted a questionnaire to all three laboratories participating in this study. Subsequent to mailing this questionnaire, the QA team visited each laboratory for an audit prior to study commencement. The audit resulted in a list of items that will assist the laboratories in their efforts to have quality data. The list of items submitted is in Appendix S as well as DPR's memorandum in response to these items.

In addition, the QA team will schedule another audit during sample analysis in each of the laboratories. A review of raw data and laboratory tracking procedures will be conducted on a minimum of 5% of all samples collected. In addition, an audit of the five highest concentrations will be conducted.

In addition, staff from U.S. EPA will conduct a flow audit in the field to verify air sampler flow rates.

6.4 Quality Control Results

A five-point calibration curve, minimum, will be run in each laboratory with each extraction set. The five points shall span the linear range of the method. Suggested working standards for 1,3-dichloropropene range from 0.05 to 10 ng/µL. Suggested working standards for chloropicrin range from 0.005 to 0.6 ng/µL. Suggested working standards for MITC range from 0.025 to 10 ng/µL, and for methyl bromide from 0.05 to 6.0 ng/µL.

New stock solutions and working standards will be generated at least every six months.

Continuing quality control samples will be run with each extraction set and will include at a minimum, two spikes (one near the low range and one near the high range of the calibration curve) and one blank. Matrix spikes will be performed in both the primary and confirmation laboratories using the same procedure (i.e., spikes will be made directly into the sorbent tubes and then extracted). Matrix spikes will be performed twice per fumigation event in the primary laboratory and twice per extraction set in the confirmation laboratory. In addition, the primary laboratory will also use solvent spikes with each extraction set.

Matrix and solvent spikes must be within warning and control limits as specified below. Two injections (duplicates) per extract will be performed. Duplicate injections on all extracts will be performed one right after the other. Duplicate injections should have a minimum precision of 15%. If greater than 15% the chemist needs to determine the reason for this result, note the problem in the laboratory notebook, and then once corrected, run a third injection to confirm the problem was rectified.

The primary laboratory will not confirm positive samples unless the acute screening level is equaled or exceeded. Mass spectroscopy is the preferred method for confirmation of such concentrations. In addition, the confirmation laboratory was established to confirm 10% of all samples collected. Where mass spectroscopy is used, intra-laboratory confirmation will not be required since this is a definitive method.

Control charts will be maintained in the laboratory for comparison with continuing quality control spikes to verify the accuracy and precision of the method. With the exception of the CDFA confirmation laboratory, a running mean plus and minus two standard deviation units will provide a warning limit. Three standard deviation units around the mean is the control limit. One spike outside the warning limit will require an examination by the chemist for potential problems with equipment, extraction procedures, analytical procedures and/or calculations. Two sequential spikes outside the warning limit will require the chemist to cease work until the problem is corrected. One quality control spike outside the control limit will cease all analytical work until the problem is corrected. Methods for establishing and using control charts in the CDFA laboratory are described in Appendix T. Samples run with extraction sets having quality control spikes outside control limits will either be re-analyzed once the problem is corrected or adjusted based on detection of a systematic error. The course of action will be discussed with the project leader at DPR.

Spikes and blanks returned to the laboratory from the field will be blind, i.e., analyte content will be unknown. Spikes and blanks will arrive with field samples, look like field samples, and their content will be unknown to the chemist.

The following describes trip spikes and fortified spikes to be generated for each

fumigation event by the primary laboratory for sorbent tubes. Four trip spikes will be prepared for each fumigation, two at an expected low concentration and two at an expected high concentration. Trip spikes for the appropriate fumigant(s) will be generated when the 24-hour notice of application is received at the laboratory. Trip spikes shall be sent overnight mail, on dry ice, to the field sampling staff address provided. Once received by field staff, all appropriate paper work and sample storage conditions will be met as described above in section 4. Trip spikes must be kept on dry ice as field staff continue with sample collection. The Supervising chemist at the primary laboratory and the project leader from DPR will agree on spike levels prior to study commencement.

Trip spikes should have recoveries equivalent to the recoveries found during method validation. Trip spikes will be compared with control charts to insure they fall within the warning and control limits, as specified above. Any deviations from this will first be investigated in the field, evaluating the shipment temperature, shipment conditions, and holding time requirements. If the source of the deviation is not in the field, an investigation will continue in the laboratory. A statistical evaluation will also be used to determine the probability of such an occurrence. If the source of the deviation cannot be found, the trip spike will be flagged in the final report, with a detailed explanation of the deviation and attempts made to clarify the deviation.

In addition to trip spikes, three fortified (sample) spikes will be generated by the primary laboratory and mailed with the trip spikes. A fortified spike is a spike that is mounted on an air sampler and run on an air sampler just like a field sample. The schedule for fortified spike sampling is located in Appendix G. The three fortified spikes will be spiked at a high concentration. The Supervising chemist at the primary laboratory and the project leader from DPR will agree on spike levels prior to study commencement.

In addition, to spikes, three trip blanks will be prepared per fumigation event by the field technician. Two trip blanks will be returned to the primary laboratory, the third will be sent to the confirmation laboratory. At the onset of sampling in the field, each laboratory (the primary and confirmation laboratory) will place a blank sorbent tube in a freezer for later analysis with incoming field samples.

Trip blanks and laboratory blanks should not contain the analytes measured (i.e., all below the method detection limit). Any deviation from this will first be investigated in the laboratory to determine if a contamination problem exists. If a contamination problem is identified, samples affected by this contamination will be flagged in the final report and the problem explained. This type of contamination generally leads to higher concentrations than actually existed in air at the time of sampling. Any adjustments to the data, if made at all, will be fully disclosed in the final report. Other sources of contamination will be investigated if laboratory contamination is ruled out, e.g.,

contamination during shipping.

A similar scheme will be conducted for canister spikes and blanks, if enough canisters are available. Currently, there are only 10 canisters and the sampling schedule for those canisters is in Appendix G. Members of the TAG decided upon the sampling schedule for 10 canisters at the Sept. 29, 1999 meeting. It is anticipated that there will be 40 canisters available prior to completion of this study. Therefore, not all spikes and blanks described above will be possible. The final number of spikes and blanks will be discussed with the primary laboratory, confirmation laboratory, U.S. EPA, and DPR.

All data reported shall go through review in the laboratory, in accordance with each laboratory's quality assurance plan or SOP, prior to submission to DPR. Signatures of the supervising chemist and/or analytical chemist(s) will verify that this review has occurred.

6.5 Laboratory Reporting

The laboratory reports shall include at a minimum, the following information:

- Analytical results for all samples, trip spikes, fortified spikes, field blanks in µg/sample. Dates of extraction and analysis will be recorded for each sample.
- The cis and trans isomers of 1,3-dichloropropene will be reported.
- Mass spectroscopy confirmation will be reported, if performed.
- Case narrative (discussion of analysis and any problems encountered).
- Chain of Custody
- Sample receipt (Log-in) Forms
- Blank sample and blank continuing quality control results
- Matrix spike results and identification of corresponding samples in the same extraction set
- Solvent spike results (if applicable) and identification of corresponding samples in the same extraction set
- Control chart warning and control limits
- Date of sample receipt
- Date of sample extraction
- Date of sample analysis

7. DATA ANALYSIS

7.1 Calculation of Air Concentrations and Concentration Reporting

Air concentrations will be calculated from the weight of analyte per sample (determined in the chemical analysis) divided by the volume of air drawn through an air sampler

during the corresponding sampling period. Concentrations will be reported in $\mu g/m^3$ and also converted to parts per billion, volume per volume. Samples below the limit of quantitation will be reported as trace. However, these samples will be assigned the value mid-way between the limit of quantitation and the method detection limit for use in all calculations. Samples below the method detection limit will be assigned the value of one-half the method detection limit when used in calculations.

The 24-hour time-weighted average concentrations will be calculated using the following formula:

24-hour time-weighted average = (2 x 16-hour concentration + 8-hour concentration)/3

Subchronic exposures will be calculated by averaging the three 24-hour time-weighted averages obtained at each site during each fumigation. The maximum three-day average over all sites and fumigations will be compared to the subchronic screening level.

The 8- and 16-hour measured concentrations, as well as the calculated 24-hour time-weighted average concentration will be reported.

7.2 Estimate Total Error

Sampling design error – The variance of the maximum 24-hour time-weighted average concentration will be estimated by computer simulation, using the parameter values estimated from the data. In addition, the likelihood that the maximum 24-hour concentration was missed will be assessed as described in section 7.4. If it is judged that the peak may have been missed, modeling will be done to estimate the maximum 24-hour concentration (see section 7.5).

Measurement error – Total measurement error is captured in the variability within pairs of colocated duplicate samples. After data collection is complete, this variance will be estimated as the within-pairs mean-squared-error in a between-pairs analysis of variance. Control limits for individual pairs, based on relative percent difference, were developed using all previous data from colocated samplers. Relative percent difference was calculated as 100*(Sample1 - Sample2)/(Mean of 2 samples). For MITC, the 95^{th} percentile of absolute relative percent difference was 41. This means that 95% of pairs were within ± 41% of each other. Control limits will be set at ± 40% relative percent difference. Pairs differing by more than 40% will be examined for possible sampling and analytical errors.

Total error – Total error variance will be estimated as the sum of the variances estimated for sampling and measurement error.

7.3 Statistical Evaluation

The null hypothesis is that the maximum 24-hour time-weighted average concentration is greater than or equal to the acute screening level of 6.6 $\mu g/m^3$ (for MITC). The null hypothesis will be rejected if the maximum 24-hour time-weighted average concentration observed for the fumigant is less than 6.6 $\mu g/m^3$.

Agreement between the primary and confirmation laboratories, between the cannister and sorbent sampling methods and between pairs of colocated samplers will be evaluated using regression analysis. In each case, a regression line will be fit to the pairs of duplicate or colocated measurements. Tests of the null hypotheses that the intercept equals zero, and that the slope equals one, will indicate the presence or absence of systematic differences between laboratories, methods or samples. The degree of scatter around the regression line will reflect the amount of random variation between them.

7.4 Weather and Pesticide Use

The date, location, number of acres treated and pounds of ai applied will be tabulated for every fumigant application from November 1996 through the end of the monitoring. Average daily weather conditions during the applications will also be tabulated, including temperature, precipitation, humidity, wind speed and wind direction (hours per day from each direction). Application and weather characteristics during the monitored applications will be compared qualitatively to those of nonmonitored applications. The objective of this comparison is to determine whether the monitored applications were representative of all applications in the season, and whether the maximum 24-hour time-weighted average concentration was likely to have been captured. In addition, the application and weather characteristics of applications during the monitoring period will be compared to those of previous years, to try to determine whether the 1999-2000 application season was similar to previous application seasons and years.

Overlay maps of pesticide use and weather conditions may be prepared to assist in this comparison.

The completeness of all data collected will be reviewed. An indication of data completeness will be provided in a final report.

The accuracy and precision of all data collected will be verified as indicated in the document above. Duplicate samples, trip spikes and blanks collected will be used to assess accuracy and precision.

7.5 Modeling

At the conclusion of air sampling, the fumigations monitored during the course of this study will be compared with historic locations of pesticide use (Table 7, Figures 6-9). If none of the fumigations monitored for each chemical are as close to the city limits as historical data indicate they can occur, modeling will be performed to estimate air concentrations expected within the city limits under this "worst-case" scenario. The U.S. EPA gaussian plume dispersion model, Industrial Source Complex Short Term model (U.S. EPA 1995) will be used to estimate the modeled concentrations. As model inputs, DPR will use the following: 1) flux rates back-calculated from application site monitoring using the procedures described in Ross, et al. 1996, or measured flux rates from other studies; 2) field location closest to the city limits, based on historical applications between 1996 and 1998; 3) highest total pounds used at the site identified in number two, and 4) weather data recorded during the monitoring period. Additional parameters and modifications to this proposed modeling scheme could be addressed in future TAG meetings.

8. PROJECT ORGANIZATION

DPR's standard project organization and responsibilities are described in SOP ADMN002.00 (Appendix U). This project is under the overall management of John Sanders. Other key personnel assigned to this project include:

Project Leader:	Randy Segawa, DPR
Senior Scientist:	Lisa Ross, DPR
Field Sampling:	Pam Wofford, DPR
Statistician:	Sally Powell, DPR
Chemical Analysis:	Steve Wall, CA Dept. Health Services
	Barbara Bates, U.S. EPA Region 9
	Cathy Cooper, CA Dept. Food and Agriculture
Quality Assurance:	Don Fitzell, Air Resources Board
	Lisa Ross, DPR
	Carissa Ganapathy, DPR

In addition, to the personnel described above and in SOP ADMN002.00, other people have key roles for this specific project. DPR formed the Lompoc Interagency Work

Group (LIWG) to assist with the project. The LIWG consists of staff from federal, state, county and city agencies, as well as community representatives. The LIWG advises DPR on overall project goals, priorities, and funding. The LIWG includes several subgroups. One of those subgroups, the Technical Advisory Group (TAG), assists DPR in the planning of pesticide air monitoring and evaluation of results.

DPR is normally responsible for all quality assurance functions for its projects. For this project, DPR has formed a multi-agency quality assurance team to assist with these functions. Don Fitzell leads the multi-agency quality assurance team. This team is responsible for auditing field and laboratory procedures (as specified in the above plan), and providing a report of their audit findings to DPR management. DPR is responsible for all other quality assurance functions described in SOP ADMN002.00 (Appendix U).

A flow diagram of the project organization can be found in Figure 10.

ACKNOWLEDGEMENT

Thank you to all members of the TAG and LIWG for their comments on the draft fumigant sampling and analysis plan, dated October 27, 1999. The above text reflects those helpful comments and suggestions. The comments, and DPR's response to those comments, can be found in Appendix V.

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Figure 1. Location of Lompoc sampling sites and weather station for fumigant monitoring.

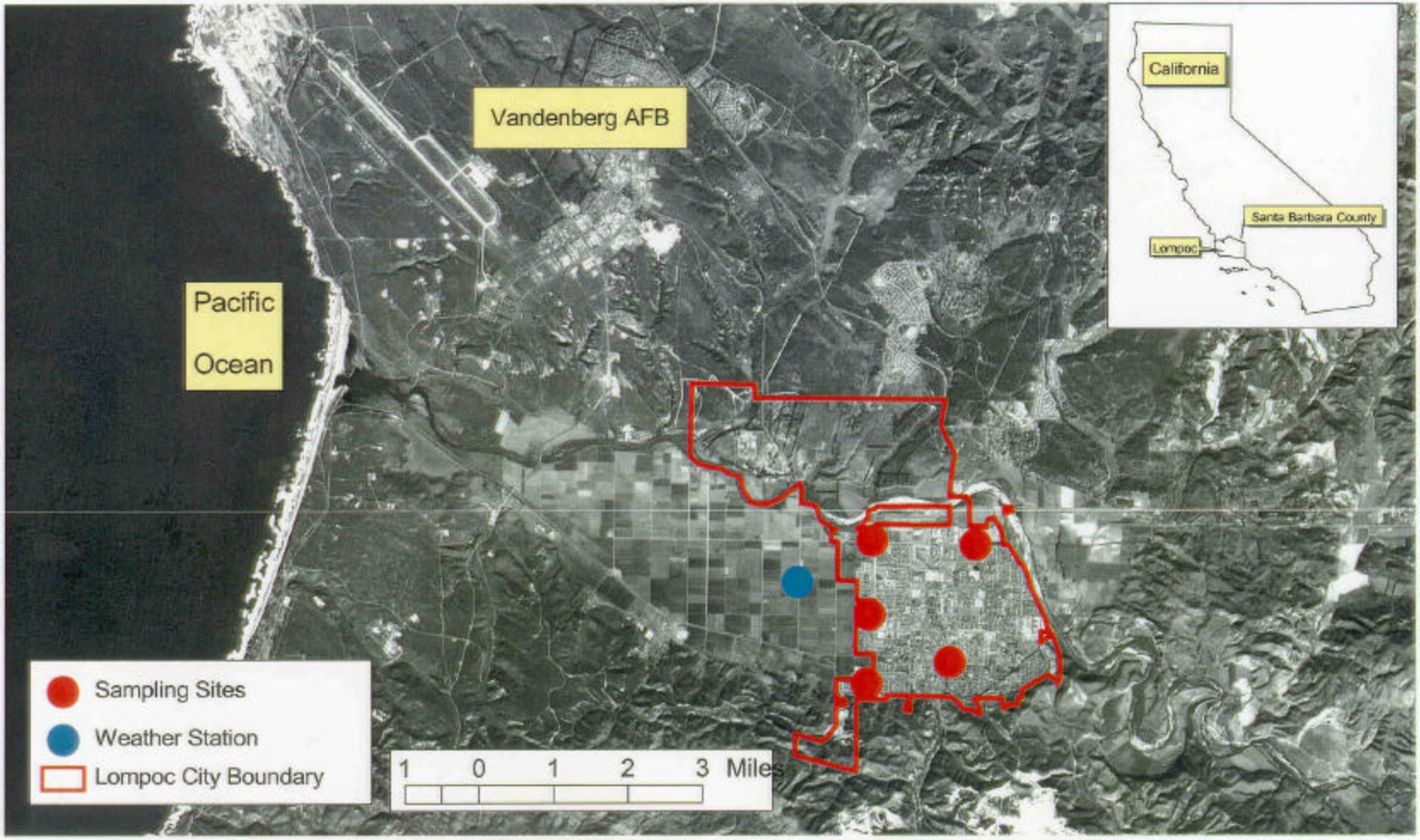

Figure 2. The percentage of time the wind blows from various directions during the months of November through January. Compiled from weather data collected during 1992-1995 at the H Street weather station located in downtown Lompoc.

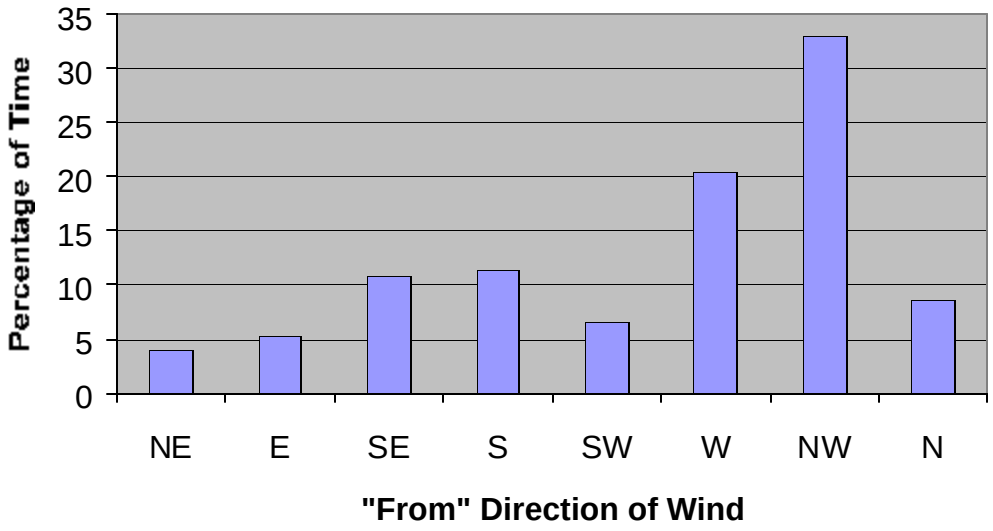

Figure 3. Township, range, and sections showing the extent of the agricultural area within which applications will be monitored.

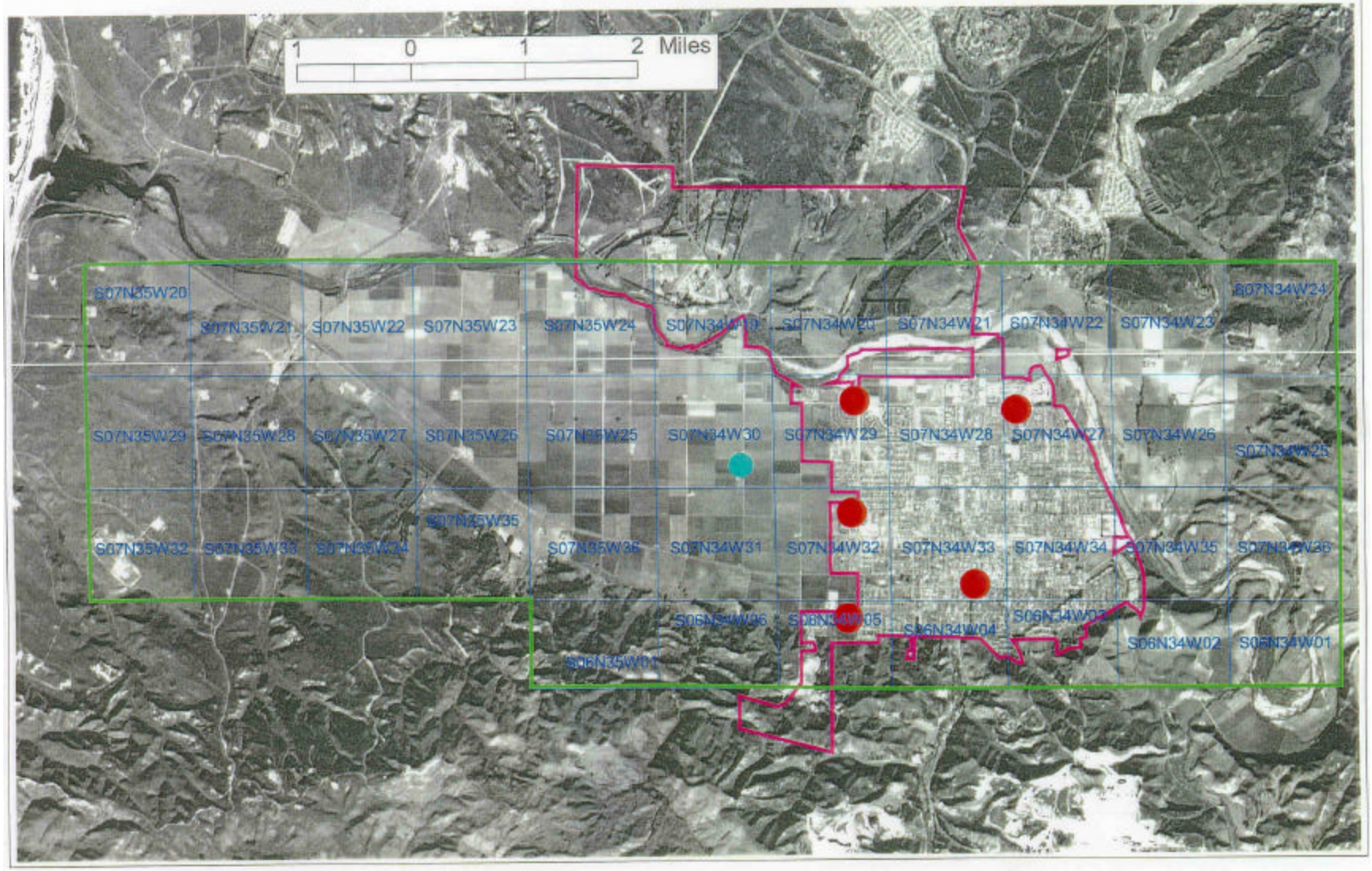

Fig. 4. Decision performance goals, power and error rates for test of the null hypothesis: MITC concentration in air ≥ acute screening level. H_0 rejected when observed maximum of 75 values < 6.6 ug m^{-3}.

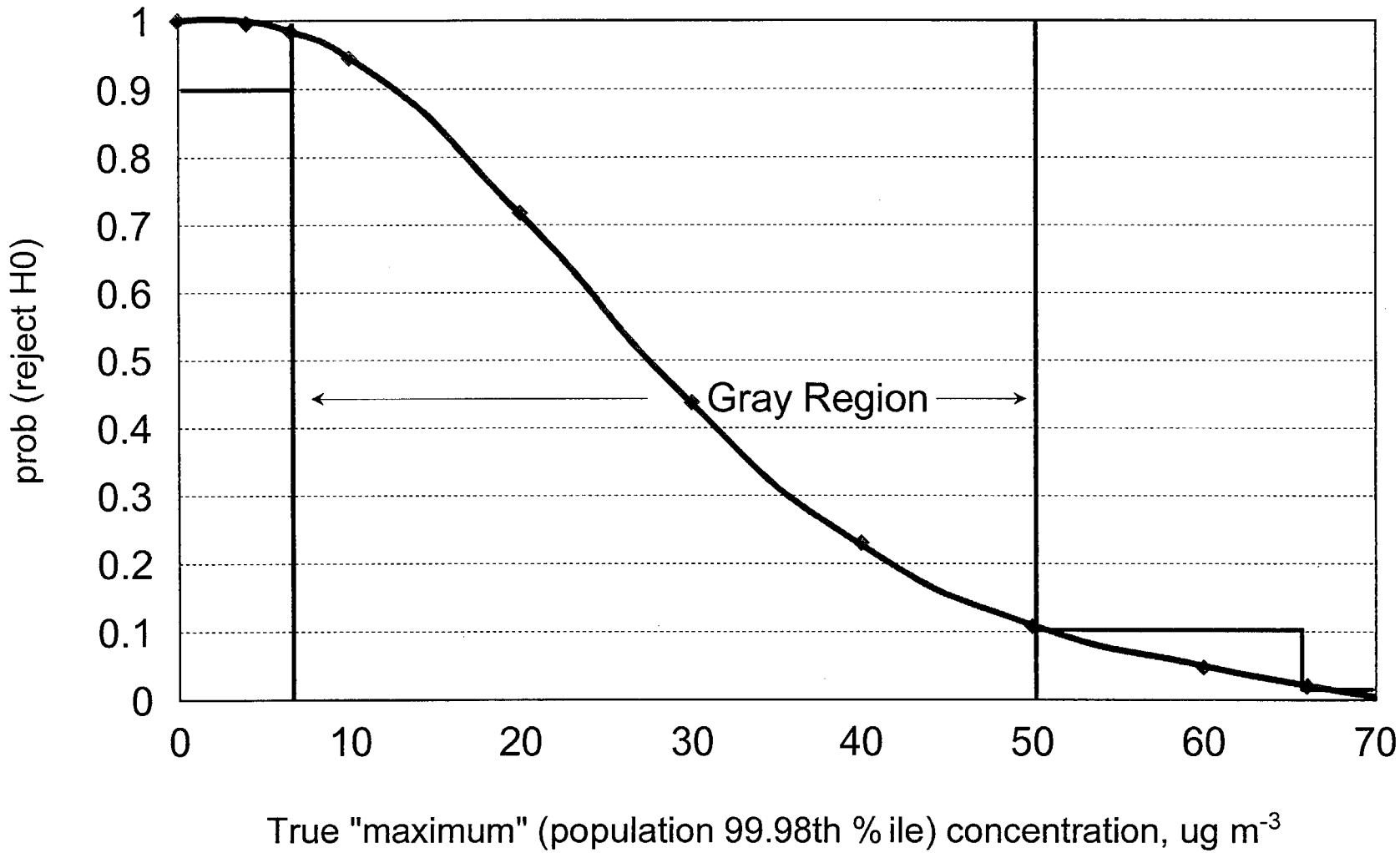

Figure 5. Township, range, and section designations in the Lompoc Valley.

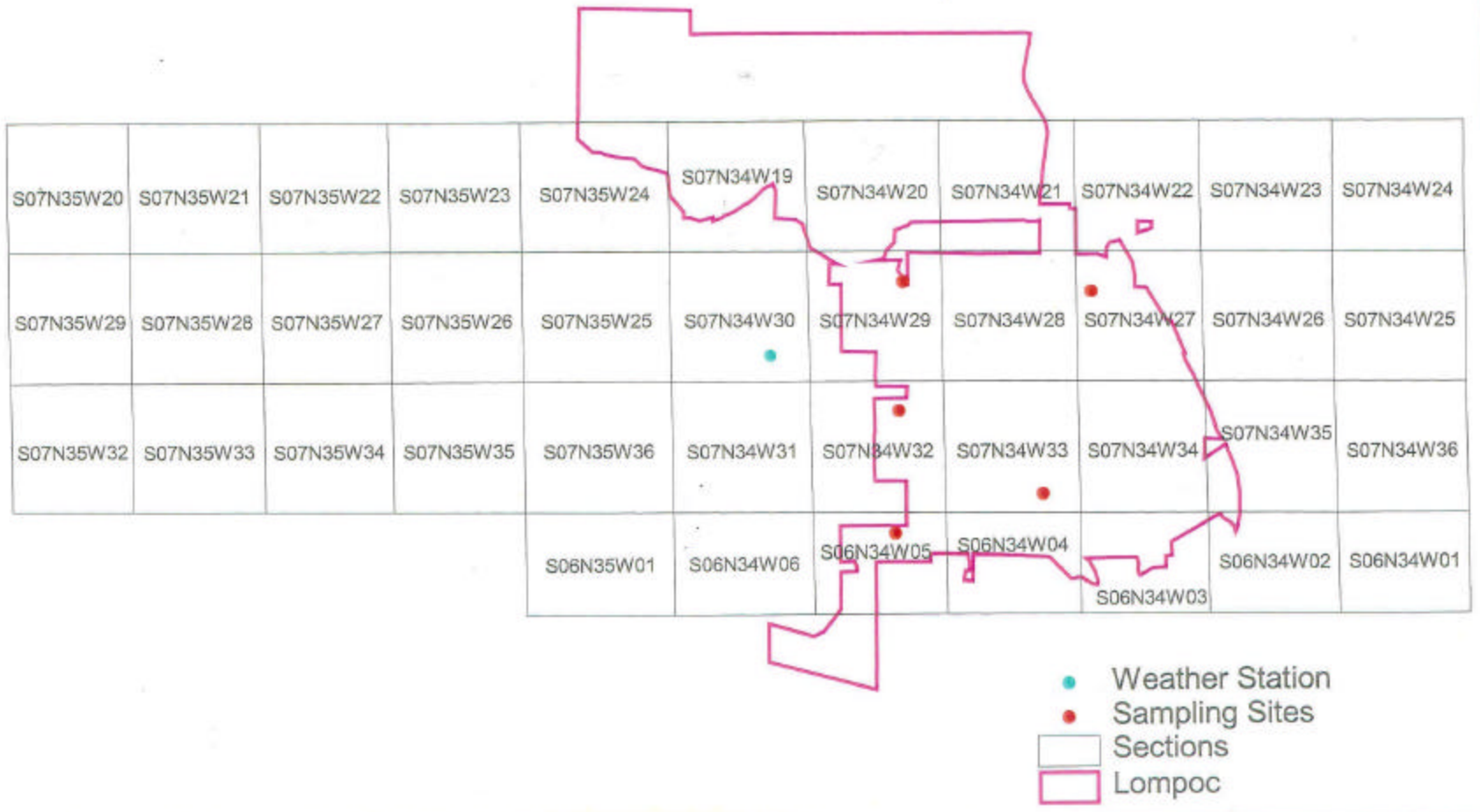

Figure 6. 1,3-Dichloropropene use reported from 1996 through 1998. Use data from 1998 are still preliminary.

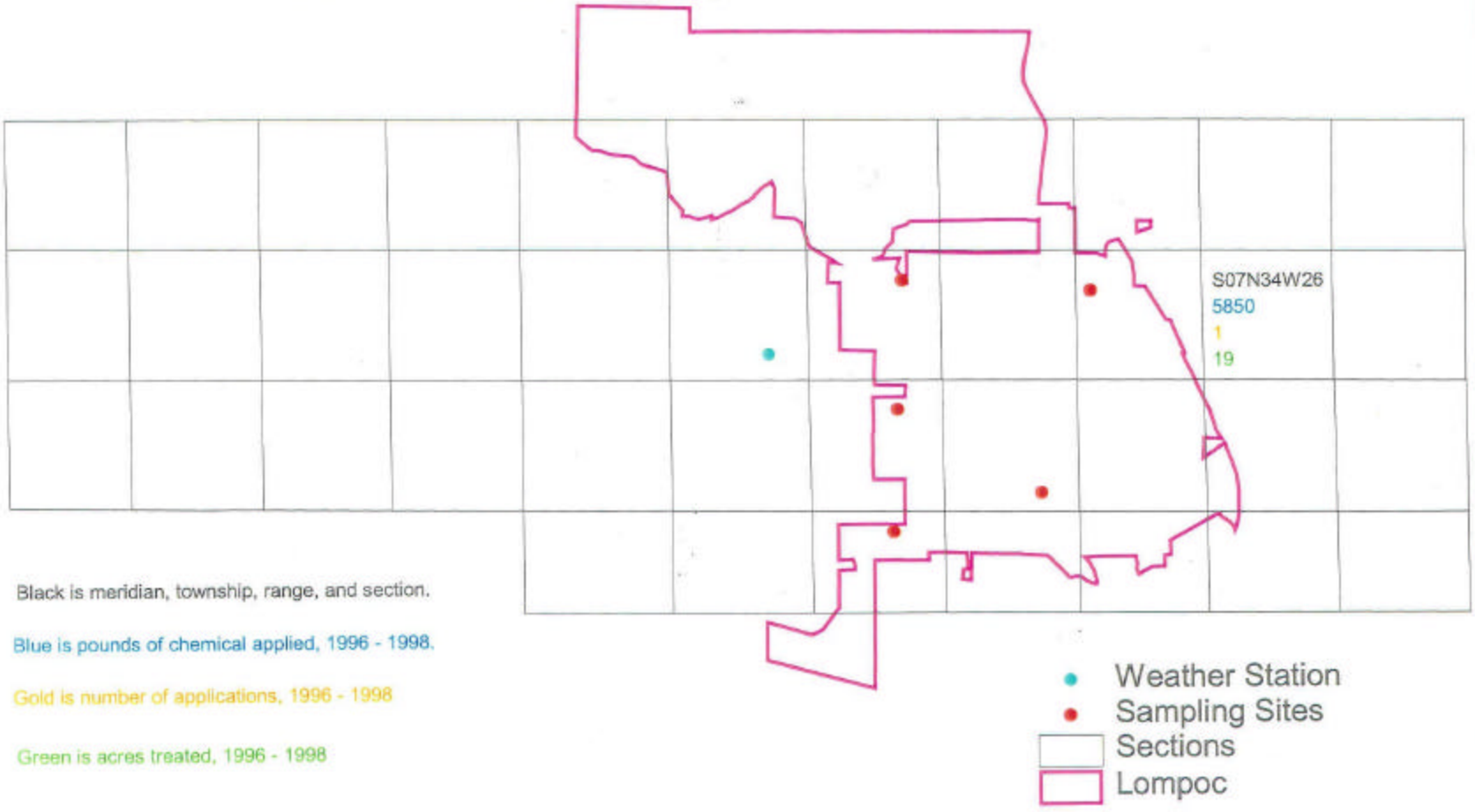

Figure 7. Chloropicrin use reported from 1996 through 1998.
Use data from 1998 are priliminary.

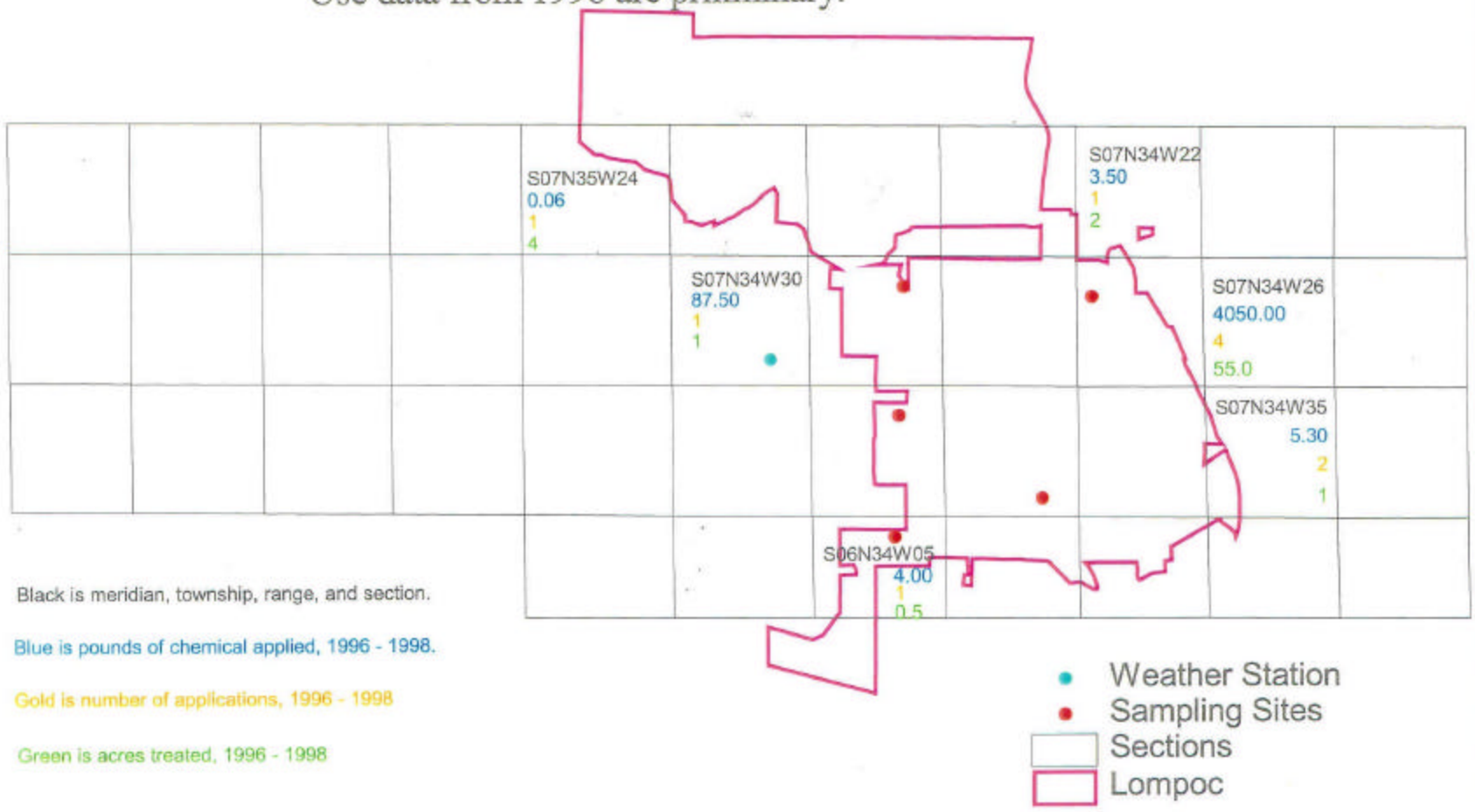

Figure 8. Metam sodium use reported from 1996 through 1998. Use data from 1998 are preliminary.

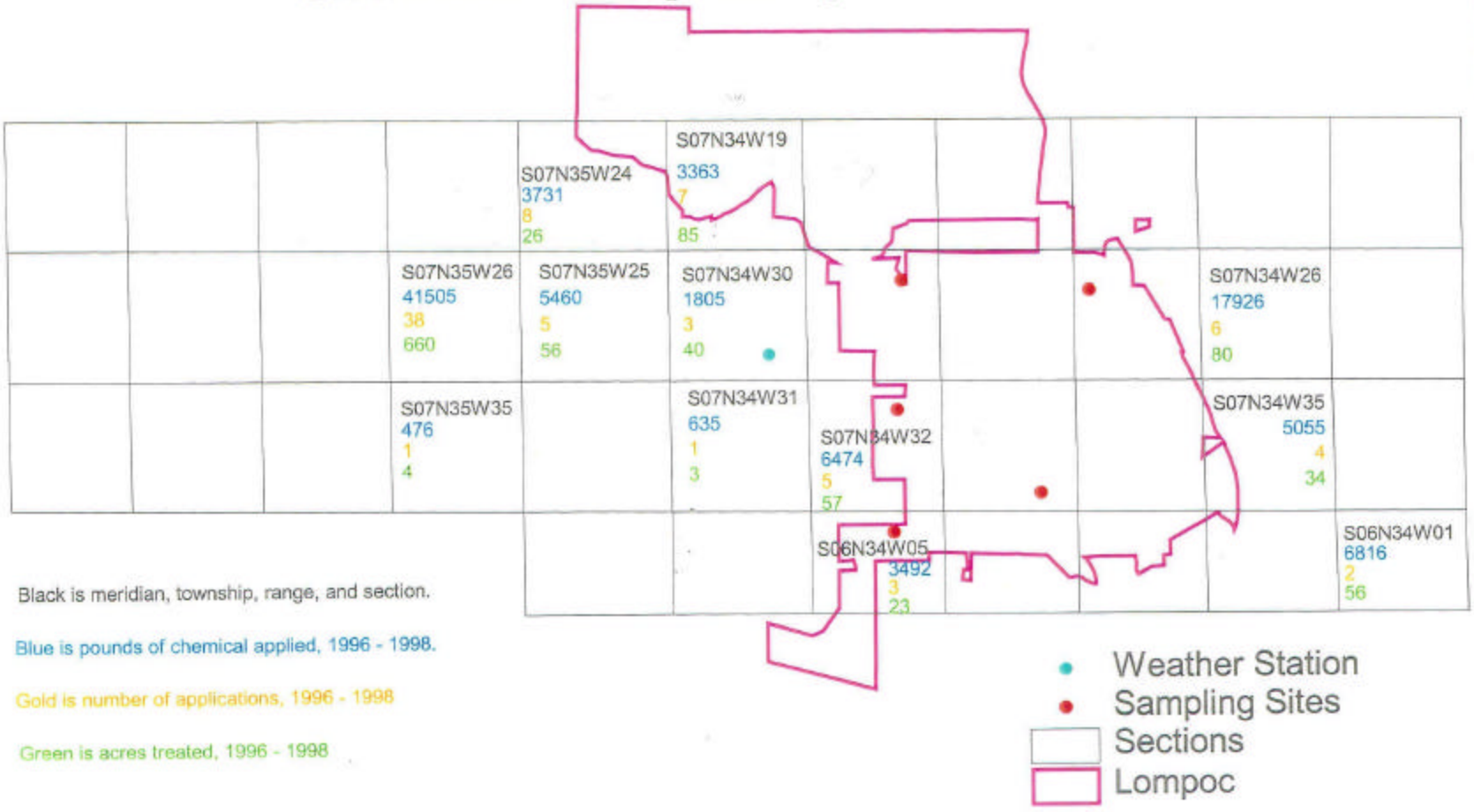

Figure 9. Methyl bromide use reported from 1996 through 1998.
Use data from 1998 are preliminary.

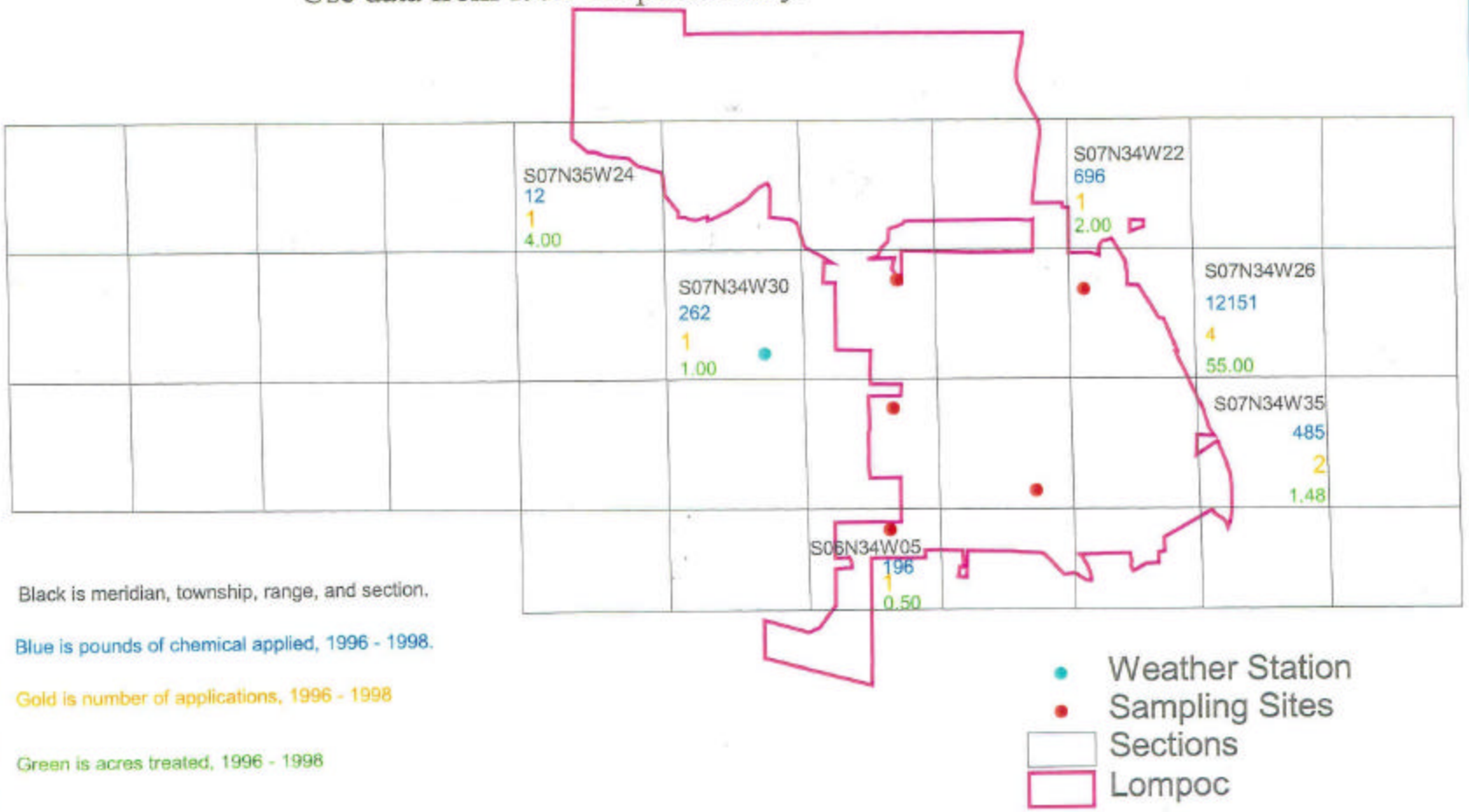

Figure 10. Project Organization

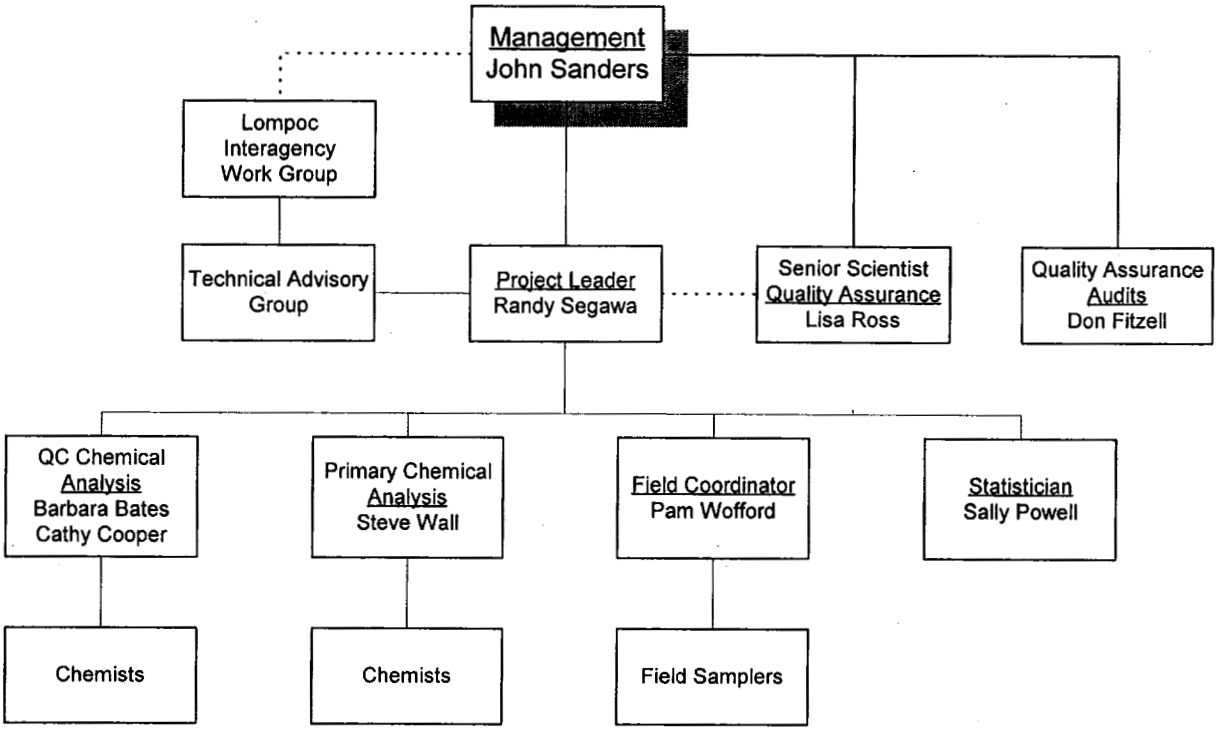

Table 1. No Observable effects levels, screening levels and recommended responses.

Analyte	No Observable Effect Level	Screening Level	Ambient Air Concentration[a]	Recommended Response[b]
Telone	**Acute (24 hour)** 14,000 $\mu g/m^3$	140 $\mu g/m^3$ (30 ppb)	< 140 $\mu g/m^3$	Not necessarily a health concern. No immediate response. May still merit further analysis.
			≥ 140 $\mu g/m^3$	Not necessarily a health concern. However, initiate a more refined analysis. If the concentration exceeds 1400 $\mu g/m^3$, immediately explore the need for mitigation measures.
	Subchronic 9,100 $\mu g/m^3$	91 $\mu g/m^3$ (20 ppb)	< 91 $\mu g/m^3$	Not necessarily a health concern. No immediate response. May still merit further analysis.
			≥ 91 $\mu g/m^3$	Not necessarily a health concern. However, initiate a more refined analysis. If the concentration exceeds 910 $\mu g/m^3$, immediately initiate explore the need for mitigation measures.
Chloro-picrin	**Acute (24 hour)** Not Available[c]	10 $\mu g/m^3$ (2 ppb)	< 10 $\mu g/m^3$	Not necessarily a health concern. No immediate response. May still merit further analysis.
			≥ 10 $\mu g/m^3$	Not necessarily a health concern. However, initiate a more refined analysis. If the concentration exceeds 100 $\mu g/m^3$, immediately explore the need for mitigation measures.
	Subchronic Not Available[c]	1.0 $\mu g/m^3$ (0.2 ppb)	< 1.0 $\mu g/m^3$	Not necessarily a health concern. No immediate response. May still merit further analysis.
			≥ 1.0 $\mu g/m^3$	Not necessarily a health concern. However, initiate a more refined analysis. If the concentration exceeds 10 $\mu g/m^3$, immediately explore the need for mitigation measures.

Table 1. Continued.

Analyte	No Observable Effect Level	Screening Level	Ambient Air Concentration[a]	Recommended Response[b]
Methyl Bromide	**Acute (24 hour)** 82,000 $\mu g/m^3$	82 $\mu g/m^3$ (21 ppb)	< 82 $\mu g/m^3$	Not necessarily a health concern. No immediate response. May still merit further analysis.
			$\geq$82 $\mu g/m^3$	Not necessarily a health concern. However, initiate a more refined analysis. If the concentration exceeds 820 $\mu g/m^3$, immediately explore the need for mitigation measures.
	Subchronic 27,000 $\mu g/m^3$	27 $\mu g/m^3$ (7 ppb)	< 27 $\mu g/m^3$	Not necessarily a health concern. No immediate response. May still merit further analysis.
			$\geq$ 27 $\mu g/m^3$	Not necessarily a health concern. However, initiate a more refined analysis. If the concentration exceeds 270 $\mu g/m^3$, immediately explore the need for mitigation measures.
MITC	**Acute(24 hour)** 660 $\mu g/m^3$	6.6 $\mu g/m^3$ (2.2 ppb)	< 6.6 $\mu g/m^3$	Not necessarily a health concern. No immediate response. May still merit further analysis.
			$\geq$ 6.6 $\mu g/m^3$	Not necessarily a health concern. However, initiate a more refined analysis. If the concentration exceeds 66 $\mu g/m^3$, immediately explore the need for mitigation measures.
	Subchronic 450 $\mu g/m^3$	4.5 $\mu g/m^3$ (1.5 ppb)	< 4.5 $\mu g/m^3$	Not necessarily a health concern. No immediate response. May still merit further analysis.
			$\geq$ 4.5 $\mu g/m^3$	Not necessarily a health concern. However, initiate a more refined analysis. If the concentration exceeds 45 $\mu g/m^3$, immediately explore the need for mitigation measures.

a. Ambient air concentrations will be averaged as described in section 7.1 of the Fumigant Sampling and Analysis Plan.
b. A more refined analysis could include, but not be limited to atmospheric dispersion modeling, more air monitoring, and a more refined risk analysis. Mitigation measures could include, but not be limited to permit conditions, statewide regulations, and label changes.
c. See memorandum text for discussion.

Table 2. Top 30 Pesticides Used for Agricultural Production in the Lompoc Area (pounds)[a].

Chemical	1996	1997	1998	Total
Metam-sodium	11251	34126	51360	96737
Fosetyl-aluminum	15841	14667	15211	45719
Maneb	10792	9028	8950	28770
Sulfur	7138	10194	8104	25435
Chlorthal-dimethyl	6804	6601	3427	16833
Iprodione	5052	4683	4460	14196
Methyl bromide	681	971	12150	13802
Chlorpyrifos	6040	4670	2847	13558
Glyphosate	1646	7227	2012	10885
Acephate	2921	2744	2293	7958
Propyzamide	2124	2587	2270	6981
Permethrin	3014	2161	1666	6841
Chlorothalonil	3654	1243	1805	6702
Dicloran	2292	2063	1877	6232
Methomyl	1963	3070	960	5993
1,3-dichloropropene	NRU	5850	NRU	5850
Simazine	4259	NRU	21	4280
Chloropicrin	9.3	91.06	4050	4150
PCNB	55	550	2793	3398
Thiodicarb	1395	1761	75	3231
Mancozeb	1231	997	999	3226
Vinclozolin	905	923	882	2710
Paraquat dichloride	226	2354	101	2681
Cryolite	1512	821	323	2656
Oxydemeton-methyl	729	1229	687	2645
Ethalfluralin	1849	381	385	2616
Bensulide	62	1425	1026	2513
Oxamyl	1188	749	556	2493
Alachlor	951	482	751	2184
Napropamide	812	208	1142	2162

a. Pesticide use data from 1998 are still preliminary.
NRU = no reported use

Table 3. Fumigants Used for Agricultural Production in the Lompoc Area, 1996 – 1998[a].

Chemical	Pounds	Acres	Applications	Year
1,3-dichloropropene	5850	19	1	97
Aluminum phosphide	3.2	NA[b]	2	96
Aluminum phosphide	7.9	NA	17	97
Aluminum phosphide	5.6	NA	16	98
Chloropicrin	4050	54	4	98
Chloropicrin	91.06	7	3	97
Chloropicrin	9.3	2	3	96
Metam-sodium	51360	415	32	98
Metam-sodium	34126	484	32	97
Metam-sodium	11251	216	19	96
Methyl bromide	12150	54	4	98
Methyl bromide	971	7	3	97
Methyl bromide	681	2	3	96
Total	120556	1260		

a. Pesticide use data from 1998 are still preliminary.
b. Not applicable. Aluminum phosphide is used primarily for commodity fumigation in closed or tarped containers or structures.

Table 4. Fumigants Used for Agricultural Production in the Lompoc Area by Month, 1996 – 1998 (pounds)[a].

Month	Aluminum phosphide	1,3-dichloro propene	Chloropicrin	Metam Sodium	Methyl Bromide	Total
January	1.3		4.06	15960	208	16173.4
February	0.9	5850		108		5958.9
March	0.9		7.30	5764	883	6655.2
April	1.2			3951		3952.2
May	1.3			13482		13483.3
June	3.6			3026		3029.6
July	0.8		1.50	571	299	872.3
August	1.7			7197		7198.7
September	1.8			6938		6939.8
October	0.8		4137.50	7440	12412	23990.3
November	0.4			21082		21082.4
December	1.8			11218		11219.8
Total	16.5	5850	4150.36	96737	13802	120556

a. Pesticide use data from 1998 are still preliminary.

Table 5. Summary of field sampling parameters and minimum chemical analytical parameters for the fumigants monitored in Lompoc December 1999 - February 2000.

	Analyte			
	1,3-dichloropropene	**chloropicrin**	**MITC**	**methyl bromide**
Sorbent Tube Adsorbent	coco. charcoal	XAD resin	coco. charcoal	pet. charcoal
Analytical Method[a]	GC	GC	GC	GC
Extraction Solvent	CS2/hexane	hexane	CS2/hexane	ethyl acetate
Detector	ECD	ECD	NPD	ECD
Trapping Efficiency	92%[b]	87%[c]	79%[d]	79%[e]
Desorption Efficiency	93%[f]	94%[c]	69-73%[d]	XY%[g]
Storage Stability	22 days[b]	42 days[c]	14 days[d]	14 days[e]
Flow Rate (L/min)	3.0	0.3	1.0	0.015
Limit of Quantitation (µg/sample)	0.xyz[b]	0.xyz[c]	0.037[d]	0.194[g]
Limit of Quantitation ($\mu g/m^3$) 8-hour			0.08	27
Limit of Quantitation ($\mu g/m^3$) 16-hour			0.04	13
Screening levels for Acute	140 $\mu g/m^3$	10 $\mu g/m^3$	6.6 $\mu g/m^3$	82 $\mu g/m^3$
Screening levels for subchronic	91 $\mu g/m^3$	1.0 $\mu g/m^3$	4.5 $\mu g/m^3$	27 $\mu g/m^3$

a. See Appendices for details.
b. See Appendix I for raw data.
c. See Appendix L for raw data.
d. See Appendix N for raw data.
e. Data from Biermann and Barry, 1999.
f. See Appendix J for raw data.
g. See Appendix P for raw data.

Table 6. Township, range and sections used to define the agricultural boundary for the Lompoc air monitoring studies.[a]

Meridian	Township	Range	section
S	06N	34W	1
S	06N	34W	2
S	06N	34W	3
S	06N	34W	4
S	06N	34W	5
S	06N	34W	6
S	06N	35W	1
S	07N	34W	19
S	07N	34W	20
S	07N	34W	21
S	07N	34W	22
S	07N	34W	23
S	07N	34W	24
S	07N	34W	25
S	07N	34W	26
S	07N	34W	27
S	07N	34W	28
S	07N	34W	29
S	07N	34W	30
S	07N	34W	31
S	07N	34W	32
S	07N	34W	33
S	07N	34W	34
S	07N	34W	35
S	07N	34W	36
S	07N	35W	20
S	07N	35W	21
S	07N	35W	22
S	07N	35W	23
S	07N	35W	24
S	07N	35W	25
S	07N	35W	26
S	07N	35W	27
S	07N	35W	28
S	07N	35W	29
S	07N	35W	32
S	07N	35W	33
S	07N	35W	34
S	07N	35W	35
S	07N	35W	36

a. See figure three for agricultural boundaries defined by the above Township-Range-sections.

Table 7. Use of four fumigants in the Lompoc Valley[a]. Data source is the Department of Pesticide Regulation Use Report database, 1996 through 1998.

CHEMICAL	MTRS	APPLICATION DATE	CROP	POUNDS A.I.	ACRES	POUNDS PER ACRE	COMMENTS
1,3-DICHLOROPROPENE	07N34W26	28-Feb-97	WALNUT (ENGLISH WALNUT, PERSIAN W	5850	19	305	
CHLOROPICRIN	07N34W35	11-Jul-96	N-OUTDR CONTAINER/FLD GRWN PLANT	1.50	1	2	
CHLOROPICRIN	07N35W24	30-Jan-97	N-OUTDR GRWN CUT FLWRS OR GREENS	0.06	4	0	
CHLOROPICRIN	07N34W22	5-Mar-97	N-OUTDR GRWN CUT FLWRS OR GREENS	3.50	2	2	
CHLOROPICRIN	07N34W30	2-Oct-97	CAULIFLOWER	87.50	1	88	
CHLOROPICRIN	07N34W26	6-Oct-98	STRAWBERRY (ALL OR UNSPEC)	750.00	10	75	
CHLOROPICRIN	07N34W26	8-Oct-98	STRAWBERRY (ALL OR UNSPEC)	2250.00	30	75	
CHLOROPICRIN	07N34W26	9-Oct-98	STRAWBERRY (ALL OR UNSPEC)	937.50	13	75	
CHLOROPICRIN	07N34W26	11-Oct-98	STRAWBERRY (ALL OR UNSPEC)	112.50	2	75	
METAM-SODIUM	07N34W26	29-Jan-96	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	2390	15	159	
METAM-SODIUM	07N35W26	29-Jan-96	CAULIFLOWER	727	6	121	
METAM-SODIUM	07N35W26	29-Jan-96	CAULIFLOWER	969	8	121	
METAM-SODIUM	07N34W30	19-Mar-96	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	112	30	4	
METAM-SODIUM	07N35W26	1-Apr-96	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	112	18.5	6	
METAM-SODIUM	07N35W26	15-Apr-96	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	112	25.5	4	
METAM-SODIUM	07N35W26	23-Apr-96	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	112	6.5	17	
METAM-SODIUM	07N35W26	11-May-96	LETTUCE, HEAD (ALL OR UNSPEC)	112	8.5	13	
METAM-SODIUM	07N35W26	18-May-96	LETTUCE, HEAD (ALL OR UNSPEC)	112	8.5	13	
METAM-SODIUM	07N35W24	4-Jun-96	N-OUTDR GRWN CUT FLWRS OR GREENS	1355	8	169	
METAM-SODIUM	07N34W32	21-Jun-96	UNCULTIVATED NON-AG AREAS (ALL OR	126	7	18	
METAM-SODIUM	07N34W32	19-Jul-96	UNCULTIVATED AGRICULTURAL AREAS	126	7	18	
METAM-SODIUM	07N34W32	19-Jul-96	UNCULTIVATED NON-AG AREAS (ALL OR	126	7	18	
METAM-SODIUM	07N34W19	20-Jul-96	CAULIFLOWER	159	18	9	
METAM-SODIUM	07N34W19	29-Jul-96	CAULIFLOWER	159	18	9	
METAM-SODIUM	07N35W24	17-Oct-96	CAULIFLOWER	423	2	212	
METAM-SODIUM	07N34W31	4-Dec-96	CAULIFLOWER	635	3	212	
METAM-SODIUM	07N34W35	21-Dec-96	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	847	5	169	
METAM-SODIUM	07N34W35	21-Dec-96	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	2540	15	169	
METAM-SODIUM	07N35W26	19-Feb-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	48	20	2	
METAM-SODIUM	07N34W19	25-Feb-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	61	16	4	
METAM-SODIUM	07N35W26	3-Mar-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	48	20	2	
METAM-SODIUM	07N35W26	7-Mar-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	48	26	2	
METAM-SODIUM	07N35W26	14-Mar-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	48	31	2	
METAM-SODIUM	07N35W26	1-Apr-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	48	15.4	3	
METAM-SODIUM	07N35W26	9-Apr-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	47	27	2	
METAM-SODIUM	07N35W26	17-Apr-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	47	20	2	

Table 7. Continued.

CHEMICAL	MTRS	APPLICATION DATE	CROP	POUNDS A.I.	ACRES	POUNDS PER ACRE	COMMENTS
METAM-SODIUM	07N35W26	23-Apr-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	47	20	2	
METAM-SODIUM	07N35W25	7-May-97	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	127	0.5	254	
METAM-SODIUM	07N35W26	8-May-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	698	15	47	
METAM-SODIUM	07N35W26	9-May-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	1693	16	106	
METAM-SODIUM	07N35W26	14-May-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	1693	16	106	
METAM-SODIUM	07N35W26	19-May-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	698	15	47	
METAM-SODIUM	07N35W25	21-May-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	1905	18	106	
METAM-SODIUM	06N34W05	23-May-97	CABBAGE	1693	10	169	
METAM-SODIUM	07N34W19	13-Jun-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	698	15	47	
METAM-SODIUM	06N34W05	18-Jun-97	SPINACH	847	5	169	
METAM-SODIUM	07N34W32	21-Aug-97	SPINACH	3725	22	169	
METAM-SODIUM	07N35W26	25-Aug-97	CAULIFLOWER	2413	19	127	
METAM-SODIUM	07N35W26	16-Sep-97	CAULIFLOWER	2032	16	127	
METAM-SODIUM	07N35W26	22-Sep-97	CELERY, GENERAL	2286	18	127	
METAM-SODIUM	07N34W30	2-Oct-97	CAULIFLOWER	635	5	127	
METAM-SODIUM	07N35W26	7-Oct-97	CAULIFLOWER	2032	16	127	
METAM-SODIUM	07N35W24	29-Oct-97	CAULIFLOWER	317	2.5	127	
METAM-SODIUM	07N35W25	29-Oct-97	CAULIFLOWER	698	5.5	127	
METAM-SODIUM	07N35W35	29-Oct-97	CAULIFLOWER	476	25	19	
METAM-SODIUM	07N34W26	20-Nov-97	CAULIFLOWER	762	6	127	
METAM-SODIUM	07N35W26	22-Nov-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	3175	16	198	
METAM-SODIUM	07N34W19	4-Dec-97	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	1016	8	127	
METAM-SODIUM	07N35W26	13-Dec-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	2032	16	127	
METAM-SODIUM	07N35W26	24-Dec-97	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	2032	16	127	
METAM-SODIUM	07N35W26	7-Jan-98	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	2032	17	120	
METAM-SODIUM	07N35W26	7-Jan-98	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	2159	22	98	
METAM-SODIUM	07N34W19	9-Jan-98	N-OUTDR GRWN CUT FLWRS OR GREENS	508	4	127	
METAM-SODIUM	07N35W25	23-Jan-98	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	1587	12.5	127	
METAM-SODIUM	07N34W26	27-Jan-98	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	3217	19	169	
METAM-SODIUM	07N34W32	28-Jan-98	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	2371	14	169	
METAM-SODIUM	07N35W26	9-Mar-98	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	63	22	3	
METAM-SODIUM	07N35W26	9-Mar-98	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	1397	5	279	
METAM-SODIUM	07N35W24	13-Mar-98	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	254	2	127	
METAM-SODIUM	07N35W24	13-Mar-98	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	444	3.5	127	
METAM-SODIUM	07N35W24	14-Mar-98	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	112	0.88	127	
METAM-SODIUM	07N35W24	14-Mar-98	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	286	2.25	127	

Table 7. Continued.

CHEMICAL	MTRS	APPLICATION DATE	CROP	POUNDS A.I.	ACRES	POUNDS PER ACRE	COMMENTS
METAM-SODIUM	07N35W24	14-Mar-98	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	540	4.25	127	
METAM-SODIUM	07N35W26	16-Mar-98	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	635	14	45	
METAM-SODIUM	07N35W26	21-Mar-98	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	1778	18	99	
METAM-SODIUM	07N35W26	4-Apr-98	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	2286	33	69	
METAM-SODIUM	07N35W25	7-Apr-98	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	1143	18	63	
METAM-SODIUM	06N34W01	8-May-98	N-OUTDR GRWN TRNSPLNT/PRPGTV MTR	4699	37	127	
METAM-SODIUM	07N35W26	15-May-98	ARTICHOKE (GLOBE) (ALL OR UNSPEC)	51	12.5	4	
METAM-SODIUM	07N34W30	15-Aug-98	CARROTS, GENERAL	1058	5	212	
METAM-SODIUM	06N34W05	10-Sep-98	BROCCOLI	952	8	127	
METAM-SODIUM	07N34W35	12-Sep-98	CAULIFLOWER	17	6.5	3	
METAM-SODIUM	07N34W35	12-Sep-98	CAULIFLOWER	1651	6.5	254	
METAM-SODIUM	07N35W26	24-Oct-98	CAULIFLOWER	1587	10	159	
METAM-SODIUM	07N35W26	30-Oct-98	BROCCOLI	1270	17.5	73	
METAM-SODIUM	07N34W19	4-Nov-98	CAULIFLOWER	762	6	127	
METAM-SODIUM	07N34W26	5-Nov-98	BROCCOLI	1905	15	127	
METAM-SODIUM	07N34W26	5-Nov-98	BROCCOLI	8636	17	508	Data flagged as outlier[b]
METAM-SODIUM	07N34W26	6-Nov-98	BROCCOLI	1016	8	127	
METAM-SODIUM	07N35W26	16-Nov-98	BROCCOLI	2222	20.5	108	
METAM-SODIUM	07N35W26	21-Nov-98	BROCCOLI	2604	3.75	694	Data flagged as outlier[b]
METAM-SODIUM	06N34W01	23-Dec-98	N-OUTDR GRWN CUT FLWRS OR GREENS	2117	19	114	
METHYL BROMIDE	06N34W05	10-Jan-96	N-GRNHS GRWN PLANTS IN CONTAINERS	196	0.5	392	
METHYL BROMIDE	07N34W35	20-Mar-96	N-OUTDR GRWN CUT FLWRS OR GREENS	186	0.48	388	
METHYL BROMIDE	07N34W35	11-Jul-96	N-OUTDR CONTAINER/FLD GRWN PLANT	299	1	299	
METHYL BROMIDE	07N35W24	30-Jan-97	N-OUTDR GRWN CUT FLWRS OR GREENS	12	4	3	
METHYL BROMIDE	07N34W22	5-Mar-97	N-OUTDR GRWN CUT FLWRS OR GREENS	697	2	348	
METHYL BROMIDE	07N34W30	2-Oct-97	CAULIFLOWER	263	1	263	
METHYL BROMIDE	07N34W26	6-Oct-98	STRAWBERRY (ALL OR UNSPEC)	2250	10	225	
METHYL BROMIDE	07N34W26	8-Oct-98	STRAWBERRY (ALL OR UNSPEC)	6750	30	225	
METHYL BROMIDE	07N34W26	9-Oct-98	STRAWBERRY (ALL OR UNSPEC)	2813	12.5	225	
METHYL BROMIDE	07N34W26	11-Oct-98	STRAWBERRY (ALL OR UNSPEC)	338	1.5	225	

a. Lompoc Valley sections were defined as described in the text and listed in Table 6.

b. Data flagged as outliers will be checked with original use reports.

Table 8. Some physical and chemical properties and break-down products of fumigants monitored in Lompoc during November 1999 through January 2000. All data are from the Department of Pesticide Regulation's Pesticide Chemistry Database, except where indicated.

Analyte	Molecular Weight	Solubility[a] in water	Vapor Pressure	Hydrolysis Half-Life	Aerobic Soil Half-Life	Photolysis Half-Life	Some Potential Atmospheric Contaminants Resulting from Degradation of the Analyte
		(mg/L)	(mm Hg)	(days)	(days)	(days)	
1,3-dichloropropene	110.98	2250	29, 25 °C	11.3, pH 7, 20 °C	11.5 - 53.9	NA	
chloropicrin	164.4	2000	23.5, 25 °C	354, pH 7, 25 °C	0.4 - 5.1	1.3[c] to 20[d]	$COCl_2$ (phosgene) NOCl (nitrosyl chloride)e
MITC	73.12	8610	16, 25 °C	20.4, pH 7, 25 °C	0.5 - 50[b]	1.1[b]	CH3NC (methyl isocyanide) CH3NCO (methyl isocyanate)
methyl bromide	94.95	1380	1420, 20 °C	17, pH 8, 25 °C	1.5 - 20	NA	methane, bromide

NA = Not applicable. The UV absorption spectra for 1,3-dichloropropene and methyl bromide are below the shortest wavelengths reaching the earth's surface (DowELANCO Study 63792, DPR Library Number 50046-33; Honaganahalli and Seiber, 1997).

a. 25 °C

b. Wales, 1999.

c. Wilhelm, et al. 1997.

d. Moilanen et al., 1978

e. These products have been measured under laboratory conditions or theorized (Moilanen, et al., 1978; Carter et al., 1997). Atmospheric measurement of these products were not found in the literature.